Multigrain

The CHEMISTRY and TECHNOLOGY of WAXES

by

ALBIN H. WARTH

Wax Research Consultant
Formerly, Chemical Director,
The Crown Cork and Seal Company
Baltimore, Md.

SECOND EDITION

REINHOLD PUBLISHING CORPORATION
New York

CHAPMAN & HALL, LTD., LONDON

Copyright 1956 by
REINHOLD PUBLISHING CORPORATION

All rights reserved

Library of Congress Catalog Card Number: 56-6695

REINHOLD PUBLISHING CORPORATION
Publishers of Chemical Engineering Catalog, Chemical Materials Catalog, "Automatic Control," "Materials & Methods"; Advertising Management of the American Chemical Society

Printed in the U.S.A. by
THE WAVERLY PRESS, INC., Baltimore, Md.

Foreword

The author's chief purpose in preparing this book has been to provide a ready reference work for chemists and industrialists who require a knowledge of waxes in their line of endeavor, and for those students and technicians who may wish to extend their background in a field with which they are not familiar.

The literature on the subject of waxes is abundant, but widely scattered. A number of textbooks on the subject of oils, fats, and waxes do exist; these, however, devote but few pages to waxes. The need for an authoritative book on the subject of waxes, alone, is at once apparent. The author has endeavored in this volume to bring together and correlate much material that is not available to one lacking the facilities of an extensive library.

The traditional organic chemistry textbooks fail to include data concerning hydrocarbons, alcohols, acids, esters, etc., of higher carbon content than those found in the fats and oils. Such high-carbon compounds are normally found as components in waxes, both natural and synthetic. Hence, the author has considered it essential to describe these compounds in detail in an extended section dealing with the chemistry of waxes. Although tabular information on such items as the keto, hydroxy and dibasic acids may appear overdrawn, it should prove useful to the investigator elucidating unknown components of a wax, or delving into the chemistry of wax metabolism in the growth of plants—a subject about which little is known.

The chemical constitution of many of the lipide waxes, even of the well known ones, is not yet fully understood, but considerable progress has been made in that direction in the last decade. Notable examples are *beeswax*, *woolwax*, and carnauba wax. The results of research in this field have been assembled here. Adequate space has also been devoted to a survey of the petroleum waxes—a study of growing importance since the introduction of the comparatively new *microcrystalline waxes*, and their emulsifiable derivatives. Similarly, considerable room has been given to the polyethylene waxes, the most important contribution in recent years in the field of synthetic waxes, made by the relatively new petrochemical industry.

The nomenclature for plant names, scientific and popular, is for the large part that approved by the American Joint Committee on Horticultural Nomenclature. The consolidating of compound names (elimination of

hyphens, e.g., jackinthepulpit instead of jack-in-the-pulpit) is the one followed by the Committee in "Standardized Plant Names," Harrisburg, Pa., J. Horace McFarland Company, 1942.

The industrial application of waxes is a subject deserving wide attention. For this reason, alone, this Second Edition gives nearly twice as much space to the use of waxes in the arts and industries as did the First Edition. All chapters of the book have been greatly enlarged, and much new material added to the tables of physical constants given in the Appendix.

Formulas given throughout the book are for the sole purpose of illustrating uses of wax; few are ideal for manufacturing purposes, although they will serve the purpose of starting the technician in formulating improved articles for industrial or consumer use.

Detailed acknowledgment of all sources of information drawn upon in the compilation of the data herein presented would not be possible within the brief space afforded, but an effort has been made to acknowledge the efforts of co-workers in the references cited at the end of each chapter. In particular, the author wishes to acknowledge the aid and encouragement given him by readers of the First Edition both here and abroad, and to firms which so willingly furnished illustrations. Thanks are also due Mrs. Jeanne B. Flagg of the Reinhold Publishing Corporation for her assistance in classifying much of the material so as to make it readily accessible to the reader.

Baltimore, Maryland
May, 1956

ALBIN H. WARTH

Contents

Page

FOREWORD iii

CHAPTER

1. INTRODUCTION 1

2. CHEMICAL COMPONENTS OF WAXES 4
Formation of Chemical Components of Plants • Role of Carbohydrates in Plant Metabolism • Formation of Waxes in Plants • Wax Hydrocarbons • Wax Alcohols • Steroids • Monobasic Fatty and Wax Acids • Unit Cell Structure • Branched-Chain Acids • Unsaturated Fatty Acids • Keto Acids • Dicarboxylic Acids • Hydroxy and Dihydroxy Acids • Lactones • Etholides • Wax Esters • Glycerides • Resins

3. THE NATURAL WAXES 76
Waxes from Insects (Beeswax, Scale Insect Waxes) • Waxes from Animals (Woolwax, Spermaceti, Liquid Waxes—Marine Oils) • Waxes from Plants (Formation in Arid Plants, Palm Tree Waxes, Candelilla Wax, Retamo Wax, Flax Wax, Cotton Wax, Hemp Wax, Sugarcane Wax, Esparto Wax, Sorghum-Grain Wax, Ricebran Wax, Leaf Blade Waxes, Waxes from Roots, Waxes from Barks, Japanwax, Myrica Waxes, Cranberry Wax, Cuticle Waxes of Fruit, Liquid Vegetable Wax, Floral Waxes) • Waxes from Microorganisms • Waxes in Cerebrosides

4. FOSSIL WAXES, EARTH WAXES, PEAT WAXES, MONTANA WAXES, AND LIGNITE PARAFFINS 342
Waxes from Low Forms of Marine Life • Ozocerite • Utahwax • Ceresin • Peat Wax • Montan Wax • Alpco Wax • Paraffin Wax from Shale Oils • Paraffin Wax from Brown Coal

5. PETROLEUM WAXES 377
Processes of Refining Petroleum • Wax Distillates • Solvent Dewaxing Plants • Crystalline Types of Petroleum Waxes • Wax Hydrocarbons • Rod Wax • Paraffin Waxes (Slack Wax, Fully Refined Paraffines) • Petrolatum • Microcrystalline Waxes • Effect of Petroleum Waxes on Metals • Antioxidants for Waxes

Page

6. SYNTHETIC WAXES 443
Classification • Polyethylene Wax • Ethylene Copolymer Waxes • Carbowaxes • Halogenated Hydrocarbon Waxes (Chlorinated Paraffin Wax, Chlorinated Naphthalenes) • Gersthofen Waxes • Polyhydric Alcohol Esters of Hydroxy Acids • Fischer-Tropsch Waxes • Hydrogenated Waxes • Waxy Ketones • Fatty Acid Amides • Imide Waxes • Polyol Ether Esters • Miscellaneous Unclassified Waxes

7. COMMERCIAL MODIFIED, BLENDED, AND COMPOUNDED WAXES .. 497
Oxidized Hydrocarbon Waxes • Vacuum-Distilled Waxes • Modified Ester Type Waxes • Emulsifiable Polyethylene Waxes • Ceresin Wax • Paraffin and Carnauba Wax Blends • Dairy Wax • Polyethylene and Petroleum Wax Mixtures • Resin and Wax Mixtures • Wax and Rubber Mixtures • Silicone and Wax Compositions • Cellulose Ether Wax • Substitute Waxes

8. EMULSIFIABLE WAXES, WAXY ALCOHOLS AND ACIDS, METALLIC SOAPS 524
Waxes with Free Alcohols • Emulsifiable Wax Stocks • Scale Wax Emulsions • OMC Waxes • Emulsifying Agents • Synthetic Emulsifiable Waxes • Polyhydric Alcohol Fatty Acid Esters • Surface-active Agents • Naphthenic Acids • Wax Emulsions for Specific Uses • Waxy Alcohols • Waxy Acids • Acids from Paraffin Wax • Eutectics of Fatty Acids • Hydroxystearic Acid • Metallic Soaps

9. METHODS FOR DETERMINING THE CONSTANTS OF WAXES 582
Determination of Chemical Constants (Saponification Number, Saponification Equivalent, Acid Value, Ester Value, Iodine Number, Unsaponifiable Matter, Hydroxyl and Acetyl Numbers, Determination of Alcohols, Hydrocarbons Analysis, Sterol Analysis, Lactone Number, Hübl Number, Reichert-Meissl Number, Polenske Number, Carbonyl Group Determination) • Determination of Physical Constants (Melting and Setting Points, Softening Point, Solidification Point, Density, Specific Gravity, Durometer Hardness, Penetration Test, Shrinkage, Refractive Index, Blocking Point Test, Tensile Strength, Viscosity, Consistency, Bending Test, Flash Tests, Electrical Constants, Solubility, Identification of Crystalline Substances, Boiling Points, Specific Rotation, Molecular Distillation, Molecular Weight Determinations, Mass Spectrometer Analysis, X-Ray Crystal Spacings, Molar Volume and Refractivity)

Page

10. WAX TECHNOLOGY—USES IN INDUSTRY 636

Wax in Adhesives • Waxes as Antioxidants • Waxes as Pour Point Depressants • Wax in Brewing Industry • Wax Candles • Wax in Ceramics • Wax in Chewing Gums • Wax in Cosmetics • Wax in Crayons and Lead Pencils • Waxes for Electrical Insulation • Wax for Explosives and Pyrotechnics • Waxes for Floors and Floor Coverings • Wax in the Food Industry • Wax in Leather and Rubber Industries • Wax in Lubricants • Wax in the Lumber Industry • Wax in Matches • Molding and Casting in Wax • • Dental Waxes • Wax Applications to Paper Products and Foils • Paper Milk Cartons • Carbon Papers • Waxes in Pharmaceuticals • Wax in Polishes • Wax Used in Printing Processes and Printing Inks • Sealing Wax • Wax in Shoe-Polish Pastes • Wax in Sound Records • Waxes in the Textile Industry • Wax in the Tobacco Industry • Wax in Varnishes and Paint Material • Oil-Soluble Colors for Waxes • Miscellaneous Uses for Wax

APPENDIX 871

Tables of Physical Constants of Waxes

ADDENDA 897

The Compounding of Waxes

AUTHOR INDEX 899

SUBJECT INDEX 909

1. Introduction

Perhaps civilized man would never have developed at all, had he not been confronted at the very beginning with things in nature which he could not possibly ignore. He then learned to utilize these phenomena to his own advantage, and later to search for others useful to his welfare. Today man has advanced to the stage of development where he is learning to combine the elements in the soil, the water, and the air to synthesize all manner of new products, some of them superior to those supplied by nature.

So it is with wax. Wax is as old as man. The Egyptians in 4200 B.C. found numerous and varied uses for beeswax. For example they used it to preserve mummies: the wrappings which encased the corpse were first dipped in a wax solution, and wax was used in sealing the coffin. Again, the sculptured portrait of the deceased, which decorated the cover of the coffin, was often modeled in wax and painted with pigmented beeswax. This process of mixing pigments with beeswax and applying it with a heated spatula was later called "encaustic." The Egyptians are also known to have made square wax writing tablets that could be rubbed down and reused. Several tablets were often fastened together with fiber; these wax tablets were the forerunners of modern books.

The English term *wax* is derived from the Anglo-Saxon *weax*, which was the name applied to the natural material gleaned from the honeycomb of the bee. When a similar substance was found in plants it also became known as *weax* or *wachs*, and later *wax*. In modern times the term has taken on a broader significance, and is generally applied to all wax-like solids and liquids found in nature, and to those that occur individually in waxes, such as the hydrocarbons, acids, alcohols, and esters, irrespective of their source or method of preparation, provided such constituents are waxlike in their properties. Certain synthetic compounds which are not waxes from the standpoint of chemical composition, but do have waxy physical characteristics, are included because of their value in technical use as wax substitutes.

Many plants produce small proportions of wax in their tissues, in their pollen, and in their seed, but it chiefly appears as an excretion upon their leaves, stems, or fruit. In some instances this secretion is abundant and is of great importance to the plant; in desert plants it provides a surface coat-

ing which retards evaporation. A number of plants produce enough wax to be of economic importance. Such is the carnauba palm of the dry arid regions of northeastern Brazil, the leaves of which are cut, dried, and beaten to detach the wax. The candelilla plant from the desert regions of Mexico furnishes a wax which is obtained by boiling its stems and leaves. The stems of the sugar cane are coated with wax, which is being recovered economically from the refuse resulting from the extraction of its sugar. Esparto grass of northern Africa is shipped to Scotland to be dewaxed so that it can be made into paper, and the wax is recovered as a by-product. Bayberry shrubs on the sand dunes of the Atlantic Coast yield a wax when these berries are boiled; the wax is used in making festive candles.

When the term *wax* is used without further designation it has been customary to cling to the old definition, namely, that produced by the domesticated bee. Formulas still call for "yellow wax" or "white wax," which are to be interpreted as "yellow beeswax" and bleached "white beeswax." In fact, both the United States and British pharmacopoeias cling to this definition, classifying these waxes as *cera flava* and *cera alba*, respectively. Paraffin wax, derived from petroleum, is simply "paraffin," or in Latin *paraffinum* (very little affinity); and natural earth wax is referred to as "ceresin." This word, like "sincere," is derived from *cera* and *sine*, meaning "without wax," or a genuine, flawless article (from the custom of concealing defects in pottery and ceramic ware by patching them with wax).

Artists have sculptured with wax from very early times; it was customary to model in wax what they later desired to cut from stone or cast in bronze. *Beeswax* has properties which allow it to be cut and shaped with facility: it melts to a limpid fluid at a low heat; it mixes with any coloring matter and takes surface tints well; and its texture and consistency may be modified by earthy matters and by oils or fats. It is these properties which make it a most convenient medium for preparing figures and models, either by modelling or casting in molds. It was so used by the ancient Egyptians, by the Greeks, and the Romans, and later in the Renaissance in Italy. In Spain beautiful wax figures of saints, distinguished in form and coloring, were achieved in the realm of religious art. The use of beeswax for anatomical studies was first practised in Florence, and in modern times has become very common. Permanent wax models, such as authentic life-size figures of famous personages of history, are found in the exhibition of waxworks of Marie Tussaud in London.

Plant, animal and mineral waxes are, in the restricted sense, compositions made up largely of nonglyceryl esters formed in nature by the union of higher alcohols with the higher fatty acids, for example, *carnauba wax*, *wool wax*, and *montan wax*. Associated with these esters are one or more of

the following components: free fat or wax acids, free monohydric alcohols and sterols, hydrocarbons, and lactones or other condensation compounds. The components vary greatly in amount in accordance with the source of the wax. Mineral wax, when derived by direct extraction from ligneous coals, contains wax esters, free wax acids, alcohols, and ketones. If obtained by destructive distillation in nature or in the refinery, the waxes contain only hydrocarbons, which are termed the end products.

Compounds that can be isolated or artificially produced from waxes are often classed as waxes, e.g., the ester *cetyl palmitate*, produced from spermaceti, or *cetyl alcohol*, produced artificially by the hydrolysis of spermaceti. The waxy state as applied to solids has been considered as an intermediate between the fatty and the resinous states. In the purification of crude waxes such as sugarcane, the procedure is to eliminate as far as possible both the fatty and resinous states.

It would seem highly desirable to include in our broad definition of wax all the waxlike substances irrespective of source, since in the art of production or reproduction we aim to have before us the whole field of waxes or waxlike substances from which we can select those which best suit our needs. Waxes are used in the arts because of their peculiar physical characteristics—seldom because of their chemical nature.

In this volume an attempt is made to bring to the reader a more thorough understanding of the chemistry of waxes, and much new informative material that will not only be of academic interest, but may well lay the ground for considerable research in a field that will become of still greater economic importance than it is today. That this is considerable is shown by the fact that in 1939 the United States alone consumed 500 million pounds of wax, 1000 million pounds in 1949, and an estimated 1500 million pounds in 1955.

2. Chemical Components of Waxes

Formation of Chemical Components of Plants

The process of building the chemical composition of a plant begins in the chloroplastid of the cell structure. Metamorphosis takes place in the living cell, or at least largely so. According to Stobbe[137], the *chlorophyll* of the plant exhibits selective absorption of the less refrangible spectrum energy, and may act either directly on the water (H_2O) and carbon dioxide (CO_2) or as a catalyst in photosynthesis, like the optical sensitizers in orthochromatic photography.

In plant metabolism there is an interaction of free radicals evolved from carbon dioxide (CO_2), water (H_2O), nitrogen (N_2) and oxygen (O_2), assisted in some instances by mineral salts as activating agents; the radicals are CO, H, N, and O. By a tagged oxygen mechanism, employing heavy oxygen (O^{18}) as a tracer in the study of photosynthesis, Ruben and his collaborators[122a] have shown that the oxygen evolved comes from the water rather than from the carbon dioxide. They stated that the net reaction for green plant photosynthesis can be represented by the equation,

$$CO_2 + H_2O + h\nu \rightarrow O_2 + (1/n)\ (C \cdot H_2 \cdot O)_n$$

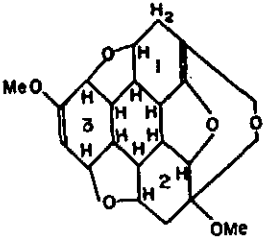
The study was made with young active *Chlorella* cells, which were suspended in heavy oxygen water (0.85 % O^{18}) containing potassium bicarbonate and carbonate. Under these conditions the oxygen exchange between the water and bicarbonate ion is slow and readily measured. Since the total amount of oxygen liberated comes from the water rather than from the carbon dioxide, the hydrogen ions freed from the water are free to react individually with the CO radical and O ion of the CO_2 to form formaldehyde (or its tautomer hydroxymethylene) and water. The vegetable plant synthesizes $C_nH_{2n}O_n$ compounds—inositols, sugars, and the like—on the basis of $nCO = nH_2$. *Methylglyoxal* ($CH_3CO \cdot CHO$) is postulated as a key substance in the formulation of lignins, tannins and pigments.

There are four types of lignin in plants: (a) simple C_6—C_3 unit; (b) simple C_6—C_3—C_6 unit; (c) reversible polymers of (a) and (b); (d) irreversible polymers of (a) and (b). Tannins and pigment originate in the plant as a result of a series of related condensation reactions between

phenols and a C_6—C_3 unit, the latter arising from the condensation reactions between methyl-glyoxal and a phenol (such as vanillin).

According to Lindgren[89] the substituted benzyl alcohols, i.e., vanillyl alcohol, veratryl alcohol (3,4-dimethoxybenzyl alcohol), apocynol [4,3-(HO)$(H_3CO)C_6H_3 \cdot CH(OH)CH_3$] and *o*-methylapocynol, are the best lignin models for studying the condensations with reactive phenols, etc., since they behave like lignin (Klasen lignin) extractable from wood with methanol. The relationship of lignin to phenols may be inferred from the fact that lignin can be hydrolyzed to coniferyl alcohol [3,-(4-hydroxy-3-methoxyphenyl)-2 propen-1-ol, m. 72–73°C] and glucose, the former being readily oxidized to vanillin (4-hydroxy-3-methoxylbenzaldehyde) and vanillic acid.

Wilstätter lignin, $C_{20}H_{22}O_6$, according to Jonas[66], has the following ring structure (C_6—C_3—C_6):



Simple lignin, $C_{18}H_{18}O_9$, has enolic groups instead of methoxy (MeO groups. Native lignin has been assigned a similar structure, $C_{22}H_{22}O_8$. Some native lignins have one MeO group, one CO group, and three OH groups, with a molecular weight of about 315. A double or polymer structure has been assigned to certain lignol derivatives, and a formula $C_{38}H_{30}O_4$ $(CO)_2 \cdot CHO\ (OH)_9$ to lignol.

By absorption of colloidal material in the sap of the plant, part of the lignin is subsequently chained to cellulose to produce woody structure. In addition to such colloidal changes, there are accompanying chemical processes such as ester formation; such hypothetical substances as cellulose hexastearate, starch hexapalmitate, inosityl tripalmitate, and the like are involved in the metamorphosis.

Role of Carbohydrates in Plant Metabolism

In the formation of carbohydrates in the plant the reduction of CO_2 and H_2 is brought about by the catalyst in the cell sap, namely *chlorophyllase*, which activates magnesium (Mg) and acts as a carrier. If the catalyst is referred to as "X" the reaction may be expressed as

$$H_2O + CO_2 + X \rightleftarrows X-(-2H)(-CO) + O_2 \rightarrow X-(-CHOH)$$

The CHOH grouping is known as *hydroxymethylene*, a tautomer of CH_2O (formaldehyde). It exists chiefly in the multiple state X $-(—CHOH)_n$; n is frequently 4. Upon desorption of the catalyst the $(—CHOH)_4$ groupings combine with free alcoholic, aldehydic and ketonic groups to form sugars, or with a —COOH to form *gluconic acid*, $CH \cdot CH_2 \cdot CH(OH)_4 \cdot CO_2H$.

Chlorophyll, a green-colored liquid found in leaf blades, is an important carrier of magnesium. This complex, $C_{33}H_{34}O_4N_4Mg$, according to Willstätter[150], is composed of magnesium, *phytol*, and a so-called phytochromin residue. Phytol, $C_{20}H_{40}$ ($b_{.03}145°C$) is an unsaturated alcohol of the same order as allyl alcohol, $CH:CH \cdot CH_2OH$, but with a long hydrocarbon chain that is branched: 3,7,11,15-tetramethyl-2-hexadecen-1-ol.[3a]

To sum up, the metabolic changes occur with chlorophyll, or its enzyme chlorophyllase, as activating agents in the chloroplastid of the cell structure, and result in the coupling of six CHOH groups to produce *inositol*, which is a hexahydric alcohol characterized by a cyclic structure. Its formula $C_6H_6(OH)_6$ has two H atoms less in the molecule than the hexitols.

The distribution of three inositols: *d*-inositol (m. 247°C), *l*-inositol (m. 247°C), and *ms*-inositol (m. 225°C) is widespread in plants and animals, and they are obviously important growth factors. If one of the H atoms of the OH groups is transposed to the adjoining C, an aldose sugar, $HOCH_2[CH(OH)]_4CHO$ is formed. A cyclizing agent, the enzyme *cyclase* in the leaves of *Lactuca virosa* L., is known to convert glucose to inositol; and in 1946 the Stettens[136] were able to secure biological conversion of *meso*-inositol into glucose.

Of the carbohydrates synthesized by plants the monoses are hexoses, namely *d*-glucose, *d*-fructose, *d*-galactose, etc., all of which have four CHOH groups. Aldoses, such as *d*-glucose have the constitution represented by the formula $OH \cdot CH_2 \cdot [CHOH]_4 \cdot CH:O$. The empirical formula for the polysacharoses is $C_6H_{10}O_5$, but they possess a much higher molecular weight, $(C_6H_{10}O_5)_n$, and are regarded as the anhydrides of hexoses and pentoses. Pentoses do not appear to exist free in the animal or vegetable kingdom, but are readily formed by the hydrolysis of various gummy carbohydrates. Polyoses such as starches, cellulose, etc. are derived in nature by the elimination of x mols of water from x mols of a monose, e.g.,

$$xC_6H_{12}O_6 - xH_2O = (C_6H_{10}O_5)_x$$

An examination of radiograms by Calvin and Benson[15], in which the path of carbon (C^{14}) was traced in photosynthesis, revealed that in the course of 30 to 90 seconds, the major portion of the reduced carbon dioxide is found in the phosphoglyceric acids, triose phosphates, and the hexose phosphates. The six-carbon hexose skeleton appears to be synthesized through the usual glycolytic intermediates. The phosphoglyceric acid through several reactions is converted to hexosephosphate. The first free carbohydrate which appears in plants is sucrose. These investigators used *Chlorella algae* as a medium for exposure to the tracer carbon dioxide, $C^{14}O_2$; they found that fructose phosphates form prior to glucose derivatives, and are the precursors of sucrose phosphate.

Just as the effect of light is to do work of a chemical nature in the formation of a substance, chemical changes can be brought about without the aid of light by unorganized ferments or enzymes, many of which act as catalysts in processes of hy-

drolysis, for example: *lipases* hydrolyze glycerides and *sterases* hydrolyze esters; *oxidases* bring about oxidation; *reductases* reduce aldoses or aldehydes to alcohols; and *carboxylases* eliminate CO_2 from carboxylic acids. The enzymes are unstable nitrogenous compounds of colloidal nature, but not necessarily proteins.

Beck[6] applied the relationship "sum of atomic volumes/molecular volume" to sugars, and found that "n $(CO + H_2)/C_nH_{2n}O_n$ approaches an optimum of the value 1, despite the fact that CO from C + O shows a maximum dilation. He was able to establish the theory by measuring the density at −5°C of numerous carbohydrates, amino acids, and hydrocarbons.

Inositol (cyclohexane hexol, inosite), which when isolated is a white crystalline powder about half as sweet as cane-sugar, was found to have a density of 1.616, or the same as galactose. Inositol occurs in plants mainly in the form of a hexaphosphoric ether called *phytic acid*, which can be isolated as the Ca or Ca-Mg salt from corn-steep liquors. Inosite hexaphosphate (phytin), according to Anderson,[3] has the formula $C_6H_6(OH)_3O_3[P_2O_3(OH)_3]_3$.

Wax Formed in Protective Cellulose Walls

According to their origin in a plant, the cellulose walls may be divided into five groups: (1) lignocellulose walls; (2) protective cellulose walls; (3) mucilage cellulose walls; (4) reserve cellulose walls; and (5) mineral cellulose walls. It is the *protective* cellulose walls that are composed of mixtures of lignocellulose, oils and waxes, and frequently contain resins or other substances as well. Just as a starch grain may attain such size as to burst through the boundary wall of the plastid to form reserve starch, the wax may exude from its border cell to form rods or granules.

Kreger[78a] has reported on the submicroscopic structure of the wax rods of sugar-cane stems. These rodlets are 0.1 mm long. Each is made up of ribbons 2000 to 5000 Å wide by 200 to 500 Å thick fastened together at their edges to form T- and similarly shaped columns. The ribbons are composed of crystallites with their long axes parallel to the length of the ribbons. The wax molecules lie crosswise to the crystallites, their long axes perpendicular to the length of the ribbons and packed as described by Müller[104].

Formation of Wax Components

The growth factors and stimulants that are instrumental in forming lignocellulose in the manner already explained function similarly in building up proteids, glycerides, and those cell-wall protective agents known as waxes. The wax components consist chiefly of alkyl esters produced by the esterification of high molecular weight alcohols with high molecular weight acids of the ethanoid series. The esters are usually accompanied by free alcohol or free acid, and by end residues of hydrocarbons of very high molecular weight.

It is well-nigh impossible to write metabolism reactions, because of the free mobile unions which can and do take place in the nascent state. It is

generally believed that the functioning elements are those of CO, H, and O, originating from the dissociation by photosynthesis of CO_2 (of air) and H_2O. In their performance these elements group themselves in multiple chains, which we call n. With $n = 4$ the solid components of waxes would be C_{12}, C_{16}, C_{20}, C_{24}, C_{28}, and C_{32}. There is invariably an even number of carbons in the methylene chain. With $n = 6$ the components would be C_{12}, C_{18}, C_{24}, and C_{30}; with $n = 8$ the components would be C_{16}, C_{24} and C_{32}. All these components are found in waxes to a varying degree. Components of higher carbon content than C_{32} are seldom met with in plant and animal waxes, since they are of too low an order of solubility to be created or perform as reactants in the cell fluid.

It is to be noted that the C_{26} and C_{31} acids, cerotic and melissic, commonly reported as wax components are not included in the metabolism groupings. Possibly both of these acids result from the elimination of CO_2 from the respective C_{27} and C_{32} dicarboxylic acids, namely tetracosylmalonic and octacosylsuccinic acid, which are known metabolism components of natural material.

Generally speaking, the components of plant waxes have an even number of carbon atoms, exclusive of sterols, keto acids, iso-fatty acids and hydrocarbons. Much difficulty is always encountered in isolating cerotic acid identical with the synthetic *n*-cerotic acid; it is also difficult to isolate melissic acid identical with *n*-melissic acid. Mixtures of C_{26} and C_{27} (iso) acids can exist beside each other in the crystal cell structure, making their separation extremely difficult or impossible. The same is true of the C_{30} and C_{31} acids. The natural C_{31} acid, melissic acid, appears to be the only *normal* straight-chain acid with an odd number of carbons believed to exist in nature, and it probably exists in a free state only in waxes.

It has been postulated that the natural acid approaching a C_{27} composition may exist as a dimeric molecule in which a normal C_{26} and an iso-C_{27} acid may be criss-crossed in the unit cell, which contains 4 molecules compacted in two pairs with COOH groups end to end, thus causing a depressed melting point, or at variance with the pure synthetic acid.

In plant metabolism it is safe to assume that alcohols (C_9 upward) are formed first. The alcohols assimilate the CO component of CO_2 to form a fatty acid, accomplished by photosynthesis of free radicals. If we designate the methylene (CH_2) chain as R′ then

$$HR'OH \rightarrow HR' \begin{matrix} \diagup CO \\ \diagdown OH \end{matrix}$$

In this manner the wax components increase in chain length. The alcohols

with *odd* number of carbons produce acids with an *even* number of carbons, and the alcohols with an even number of carbons become esterified by the acids. Any surplus of alcohols of even carbons remains free.

Representing R_m of the alcohol as a methylene chain with an *even* number of carbons and R'_n of the acid as a chain with an *odd* number of carbons, and lengths of chains as m and n, which may be equal to or different from each other, we can write the formation of esters as follows:

$$HR_m{\cdot}OH + HR'_n \begin{matrix} CO \\ \diagdown \\ OH \end{matrix} \longrightarrow HR'_n \begin{matrix} CO \\ \diagdown \\ OR_mH \end{matrix} + H_2O$$

alcohol *acid* *ester* *water*

Hydroxy acids with a terminal OH group, namely omega (ω) hydroxy acids, are formed by photosynthesis by the introduction of both O and CO in an alcohol having an odd number of carbons (C_9 and upward). They are known as *anolides* when cyclized by loss of H_2O to a lactone formation.

$$HR'_z{\cdot}OH + CO + O \rightarrow HOR'_z \begin{matrix} CO \\ \diagdown \\ OH \end{matrix} \longrightarrow \overline{OR'_z{\cdot}CO} + H_2O$$

alcohol *hydroxy acid* *anolide*

Hydrocarbons are formed by the decarboxylation of esters, the removal of the CO_2 resulting in a hydrocarbon with an *odd* number of carbons:

$$HR'_n{\cdot} \begin{matrix} CO \\ \diagdown \\ OR_mH \end{matrix} \longrightarrow HR'_nR_mH + CO_2$$

ester *hydrocarbon*

Alcohols of the *n*-long-chain primary type appear to be the main constituents of many of the plant waxes, according to an x-ray study of wax coatings of plants made by Kreger[78] of the University College of Technology, Delft, Netherlands. A few of the plant waxes of sixty studied contain *secondary alcohols*, with the OH group at the midpoint or ⅓ point of the chains. The secondary alcohols range from C_{25} to C_{31}. *Ketones* are, however, difficult to distinguish from secondary alcohols in fragmentary residues by x-ray diffraction methods. Origin of the secondary alcohols appears to be in the triple unsaturated series.

Dihydric and *trihydric alcohols*, as exemplified by the glycols and glycerol respectively, belong mostly to the vegetable and animal oils. *Polhydric*

alcohols (polyols) have the general formula $CH_2OH(CHOH)_nCH_2OH$, where n has the value of 2 or 5. Examples of polyols are erythritol (m. 120°C), which is a *tetritol* that occurs in lichens, algae and yeast; and pentaerythritol (m. 260°C), which has not been found in nature. The *pentitols* and *hexitols* occur in plant life but are not constituents of plant waxes. The *inositols* are hexihydric alcohols which are cyclized and are growth promoters. *Heptitols* are of purely academic interest.

Unsaturated higher aliphatic alcohols exist as constituents of liquid waxes of both animal and vegetable origin. *Cyclic alcohols* (nonterpenic) are found in several of the floral waxes. *Sterols* appear in the unsaponifiable residues of quite a few waxes. They are unsaturated cyclic secondary alcohols having a phenanthrene skeletal base. *Resinols* of triterpenoid structure are encountered in many of the natural resinous waxes. *Ketonic alcohols* rarely occur in waxes, but *ketones* and *lactones* are occasionally found as components of natural waxes.

Esters, also referred to as *simple esters*, *acid esters*, and *hydroxy esters*, are the more important constituents of almost all the natural waxes. A natural wax normally contains more mols of acids than of alcohols, and invariably all the alcohols are found in the combined state as esters; the acids of lower molecular weight are the first to combine with the higher alcohols, and the excess of the higher acids is left free or uncombined. Esters are actually products of metamorphosis in which the alcohols and acids unite, with elimination of a mol of water. The melting point of an ester is somewhat higher than that of the corresponding acid, and is influenced by the melting point of the alcohol to which the ester acid has been linked. All known esters in waxes have an even number of carbon atoms. Less than fifty esters have been positively identified as wax components. The natural esters often include hydroxy esters, as for example those of beeswax, carnauba was, ouricury wax, etc.

In the alcoholysis (ester-alcohol interchange) of an ester, as in hydrolysis, the alkoxy group remains intact; the bond between the —OR group and the carbonyl (CO) carbon atom is the one that is broken. In this manner the methylene chain is lengthened, e.g.,

$$RCOOR' + R''OH \rightleftharpoons RCOOR'' + R'OH$$

Or in acidolysis (ester-acid interchange),

$$RCOOR' + R''COOH \rightleftharpoons RCOOH + R''COOR'$$

Or in ester-ester interchange,

$$RCOOR' + R''COOR''' \rightleftharpoons RCOOR''' + R''COOR$$

Hydrocarbons of particular interest in natural waxes, both plant and animal, are those of the saturated open-chain series (*alkanes*) that range

from about 19 to 31 carbon atoms. Peculiarly, these hydrocarbons have an odd number of carbon atoms. Marine liquid waxes contain unsaturated hydrocarbons (*olefins*), which as a rule have far lower melting points than the saturated hydrocarbons. The melting point of a hydrocarbon increases in a regular manner with the number of carbon atoms it contains, and thus affords considerable assistance in identifying the hydrocarbon when isolated from the wax. Hydrocarbons ranging from 17 to over 44 carbons, both odd and even, are the chief constituents of the mineral and petroleum waxes. Many of them are of the branched-chain type. Unsaturated hydrocarbons are occasionally found as constituents of natural waxes, and usually have an even number of carbons. Olefins, in the generic sense, include compounds containing one or more double bonds. Olefins of C_nH_{2n} structure are termed *alkenes*.

In the formation of fat in an oleaginous fruit like the olive, the primary substance is an alcohol (oleanol), which is elaborated in the leaves and passes into the fruit; the oil must be regarded as a waste product. In the first stage of development the alcohol forms almost the whole of the fatty matter (ether extract). As the ripening of the fruit progresses, the proportion of oleanol diminishes, with corresponding increase first of fatty acids and later of glycerides. However, in the formation of oil in oleaginous seeds and in woody plants, the fats are formed from carbohydrates and act as reserve food products. The vegetable tallows (so-called waxes), as that of the bayberry, also develop after the fruit, and the active formation of cellulose, proteins, pentosans, etc., by the influx of waxy alcohol, formation of fatty acids, and lastly the formation of triglycerides, as a coating on the fruit. For constitution of the triglycerides see p. 69.

Saturated Hydrocarbons

Normal Paraffins. The straight open-chain saturated hydrocarbons, or normal alkanes, which have a melting point higher than 0°C, together with their melting points, densities of the melts, and refractive indices are given in Table 1. The fully refined paraffin waxes are believed to be made up largely of *n*-paraffin solids, ranging between C_{17} and C_{34}. The density of solid normal paraffins at room temperature is given theoretically by the equation:

$$1/D_{\text{solid}} = 1.018 + 1.465/n$$

where n is the number of carbons. For example, by this equation we arrive at a density of 0.9245 for the C_{23} hydrocarbon, 0.9268 for C_{24}, 0.9309 for C_{26}, 0.9326 for C_{27}, and 0.9341 for C_{28}. The measured density of the hydrocarbons is a trifle lower than the theoretical density because of a small amount of occluded air. C_{17} has a density of 0.9056, and C_{34} a density of 0.9425.

TABLE 1. SATURATED HYDROCARBONS: NORMAL ALKANES

Hydrocarbon	C_nH_{2n+2}	Melting Point (°C)	Density (D^t)		Refractive Index at 90°C[97]
			at M.P.	at 90°C[97]	
Tetradecane	$C_{14}H_{30}$	5.5	0.765	0.7137[p]	
Pentadecane	$C_{15}H_{32}$	10.0	0.769	0.7198[p]	
Hexadecane	$C_{16}H_{34}$	18.1, 20.0[f]	0.775	0.7253[p]	1.4345 @ 20
Heptadecane	$C_{17}H_{36}$	22.5, 20.0	0.777	0.7300[p]	
Octadecane	$C_{18}H_{38}$	28.0[a, f], 27.9	0.777	0.7344[p]	
Nonadecane	$C_{19}H_{40}$	32.0[b], 31.9[x]	0.777	0.7383[p]	
Eicosane	$C_{20}H_{42}$	37.1[m], 36.5[x], 38[f]	0.7775[x]	0.7419[p]	1.4348 @ 20
Henicosane	$C_{21}H_{14}$	40.3[c], 40.1[x]	0.7778[x]	0.7468	1.4160
Docosane	$C_{22}H_{46}$	44.3[x], 43.8[g]	0.7776[x]	0.7480[p]	
Tricosane	$C_{23}H_{48}$	47.3[c, x]	0.7779[x]	0.7431	1.4190
Tetracosane	$C_{24}H_{50}$	52.2[m], 51.0[x]	0.7781[x]	0.7562	1.4205
Pentacosane	$C_{25}H_{52}$	55.8[c], 54.6[m], 53.9[x]	0.7785[x]	0.7560[p]	
Hexacosane	$C_{26}H_{54}$	57.5[m], 56.9[x], 56.1[g]	0.7787[x]	0.7581[p]	
Heptacosane	$C_{27}H_{56}$	59.5[a, b, h, i, j]	0.7789[x]	0.7602[p]	
Octacosane	$C_{28}H_{58}$	62.4[m], 61.25[c]	0.7792[x]	0.7619[q]	1.4248
Nonacosane	$C_{29}H_{60}$	63.5[j], 64.0[b, x]	0.7797[x]	0.7639	
Triacontane	$C_{30}H_{62}$	66.6[m], 65.8[c], 65.5[g]	0.7797[x]	0.7676	1.4266
Hentriacontane	$C_{31}H_{64}$	68.1[m], 68.3[i]	0.7799[x]	0.7709	1.4278
Dotriacontane	$C_{32}H_{66}$	71.3[m], 71.0[k], 70[r]	0.7801	0.7696[r]	
Tritriacontane	$C_{33}H_{68}$	71.8, 72[b]		0.7701[p]	
Tetratriacontane	$C_{34}H_{70}$	73.3[m], 72.6[c], 72.4[g]	0.7806[x]	0.7728	1.4296
Pentatriacontane	$C_{35}H_{72}$	74.6[g], 74.0[x]	0.7813[x]	0.7734	1.4301
Hexatriacontane	$C_{36}H_{74}$	76.6[m], 76.0[x]	0.7819[x]	0.7753	1.4308
Tetracontane	$C_{40}H_{82}$	81.4[m], 80.8[q]	0.7830	0.7780[p]	
Dotetracontane	$C_{42}H_{86}$	84.9		0.7800[p]	
Tritetracontane	$C_{43}H_{88}$	85.3[c]		0.7812	1.4340
Tetratetracontane	$C_{44}H_{90}$	88.0		0.7817[p]	
Pentacontane	$C_{50}H_{102}$	92.0, 92.1[q]		0.7856[p]	
Tetrapentacontane	$C_{54}H_{110}$	95.0[a]		0.7878[p]	
Heptapentacontane	$C_{57}H_{116}$	96.5[l]		0.7894[p]	
Hexacontane (Dimyricyl)	$C_{60}H_{122}$	98.9[q]		0.7907[p]	
Dohexacontane	$C_{62}H_{126}$	101.0, 100.5[g]		0.7916[p]	
Tetrahexacontane	$C_{64}H_{130}$	102.0[a, g]		0.7937[g]	
Hexahexacontane	$C_{66}H_{134}$	103.6 (crystal spacing 87.84 Å)			
Heptahexacontane	$C_{67}H_{136}$	104.1[d]		0.7935[p]	
Heptacontane	$C_{70}H_{142}$	105.2, 105.3[q]		0.7945[p]	

[a]Melting point by Gascard[46]; [b]m.p. by Hildebrand and Wachter[56]; [c]m.p. by Mazee[97]; [d]m.p. by Francis *et al.*[40]; [e]m.p. by Brigl[14]; [f]m.p. by Levene *et al.*[86]; [g]setting point by Garner *et al.*[44]; [h]m.p. by Gottfried and Ulzer[47]; [i]m.p. by Lipp and Kovács[80]; [j]m.p. by Damoy[28a] from natural source; [k]m.p. by Meyer and Soyka; [l]m.p. by Carpenter; [m]mean value of several investigators; [x]Krafft's vacuum-distilled hydrocarbons from specimen of hard paraffin (m. 80°C) prepared from Saxon brown coal[77]; [p]computed from the formula:

$$1/D = 1.143 + 0.00089 + 1/(0.500 - 0.00110t)n$$

where D is the density of the liquid (melt) normal paraffin, with carbon n at temperature t; [q]mean of m.p. range of Carothers *et al.* (1930)[16]; [r]by Delcourt (1931)[28a]. [s]by Monick *et al.*[102]

Müller[104] reported on an x-ray investigation of a single crystal of the natural hydrocarbon $C_{29}H_{60}$ as a typical geometric structure. The crystal belongs to the orthorhombic space group Q_H^{16}. The unit cell has the dimensions $a = 7.45$ Å, $b = 4.97$ Å, $c = 77.2$ Å (error approx. ½ %). There are 4 molecules to a unit cell. The cross-section area occupied by one molecule is 18.5×10^{-18} sq cm. The gap between the ends of two consecutive molecules in the crystal, measured along the c axis, is 3.09 Å.

All paraffins in the range of C_{17} to C_{34} exist near the melting point in a form suggesting closely packed hexagonal pencils. On cooling, the form changes to a stable one at a fixed transition point. Transition points (in °C) for many of the higher hydrocarbons have been established by Mazee[97]: C_{21} 32.8, C_{23} 40.6, C_{24} 47.0, C_{28} 54.2, C_{30} 59.2, C_{31} 61.8, C_{35} 71.6, C_{36} 73.5. Boiling points of the normal alkanes are given in Table 2.

The following constants were established by Mlle. Delcourt[28a] for the $C_{32}H_{66}$ hydrocarbon: melting point 70°C; density (d^{75}_4) 0.77910, (d^{100}_4) 0.76321, (d^{118}_4) 0.75185; viscosity (η^{75}) 0.0658, (η^{100}) 0.0409 CGS units; freezing point constant 5.5°C; molecular heat of fusion 42.5 cal; solubility in water about 0.01 per cent at the m.p.; the hydrocarbon decomposes slightly on distillation.

There are three stable modifications of the normal C_{24} hydrocarbon, namely hexagonal at 46.5°C, monoclinic at 42°C, and triclinic at room temperature[97]. The crystallographic behavior of other alkanes is similar, with two or more modifications when the transition points are reached.

Branched-Chain Paraffins. Associated with petroleum waxes are a number of cyclic and/or branched solid or semi-solid hydrocarbons. In general the branched alkanes have appreciably lower melting points than the normal alkanes. For example, whereas normal hexacosane melts at 56.2°C[23], paraffins with the empirical formula $C_{26}H_{54}$ and a butyl side chain have much lower melting points: 5-*n*-butyldocosane 20.8°C, 7-*n*-butyldocosane 3.1°C; 9-*n*-butyldocosane 1.3°C. 1-*n*-Hexacosane crystallizes in rhombic plates and twinning parallelogram plates; the butyl branched chain hydrocarbons crystallize similarly.

Examples of C_{24} branched chains are *2-methyltricosane* ($C_{24}H_{50}$) and *2,2-dimethyldocosane* ($C_{24}H_{50}$) which melt at 37.6 and 34.8°C, respectively.

Of the branched-chain hydrocarbons, the so-called isoalkanes have the alkyl group in the preultimate position, for example, isotetracosane is *22-methyltricosane*. The isoalkanes have melting points which are generally a trifle higher than those of the corresponding normal alkanes; for example, isotetracosane (22-methyltricosane) melts at 51–51.5°C[85], whereas normal tetracosane melts at 50.7°C. Isotetracosane has been prepared from the lignoceric acid obtained from natural sources[85]. *Cerane*, from isoceryl alcohol, is isohexacosane (b_7 207°C), and melts at 61°C[86], contrasted to 56.1°C

TABLE 2. BOILING POINTS OF SATURATED HYDROCARBONS: NORMAL ALKANES

Hydrocarbon C Number	°C Boiling Point at Pressure of 760 mm	15 mm	3 mm	1 mm	0.1 mm
14	252.5	129.5			
15	270.6	144.0			
16	286.5	157.0		$110.0_{1.9}$[a]	
17	295.5	170.0			
18	301.4	181.5, 177.0[a]	169.5		
19	305.0	193.0			109.0[x]
20	309.7[d]	205.0		$148.0_{9.6}$[a]	117.5[x]
21	313.4	215.5	179.8[b]		125.5[x]
22	317.4	224.5			130.5[x]
23	320.7	234.0	199.5[b]		138.0[x]
24	324.3	243.0	208.6[b]		145.5[x]
		237–240[c]			
25	327.4[f]	254.0			152.5[x]
26	330.3[f]	262.0		205.0[b]	160.0[x]
27	332.5	275.0			167.0[x]
28	335.7[f]	286.0	242.0[b]	$224.0_{1.1}$[a]	173.5[x]
29	338.1[f]	295.0			179.0[x]
30	338.5[i]	304.0	258.5[b]	235.0[a]	186.0[x]
31	341.1	310.0	266.2[b]		193.5[x]
32	343.5	319, 310[a]		$245.0_{1.5}$[a]	201.0[x]
33		328.0			
34	345.4[i]	336.0	285.4[b]	255.0[a]	215.0[x]
35	347.0[i]		292.3[b]		222.0[x]
36	349.0		298.4[b]	265.0[a]	230.0[x]
38	351.2				
					10^{-5} mm
40	353.8			241.0	150[k]
43			332.0[b]		
50	365.1				200[k]
60	371.0				250[k]

Note: B.p. of C_{24} hydrocarbon is 199.0°C at 0.4 mm[a].

[a]Boiling point of Levene *et al.*[86]; [b]b.p. by Mazee[97]; [c]b.p. by Levene and West[85]; [x]Krafft's vacuum-distilled hydrocarbons; [d]b.p. by Gascard[46]; [f]computed by formula: $\Delta_n = \frac{85 - 0.01882(n-1)^2}{n-1}$, where n = number of carbons; [h]b.p. by Clarke, E. W.[22]; [g]by Meyer, Brod and Soyka (1913)[100]; [j]b.p. by King, A. M. (1931); [k]b.p. by Carothers *et al.* (1930)[16]; [x]b.p. by Carothers *et al.* (1930)[16]; b.p. C_{70} hydrocarbon is 300°C at 10^{-5} mm pressure.

for the normal hexacosane. Isoöctacosane has been isolated from the herb *Alchemilla alpina* L., commonly known as mountain ladysmantle; it melts at 70°C, whereas normal octacosane melts at 61.3°C. Isopentacosane melts at 56°C.[84]

According to Levene *et al.*[86], *melissane*, derived from melissyl alcohol

obtained from natural sources, is isotriacontane ($b_{0.3}$ 222°C) and melts at 73–74°C; normal *triacontane* melts at 65.5°C. The hydrocarbons commonly found in plants have a normal chain structure; the most common one is *n-hentriacontane*, $C_{31}H_{64}$.

Normal *tetracontane*, $C_{44}H_{90}$, melts at 88°C; but with a CH_3 linkage near the center of the polymethylene chain as in 22-methyltritetracontane ($C_{44}H_{90}$), the melting point is depressed to 66.6°C. If the alkane has a forked chain with a long alkyl group the melting point is very low; for example, 10-nonylnonadecane ($C_{28}H_{58}$) melts at −5°C, whereas the normal alkane melts at 61.2°C[97].

The boiling points of branched-chain paraffins having only methyl groups as substituents, according to Kozlov[73], can be calculated from the boiling points of the corresponding *n*-paraffins, and certain increments applied depending on the distance of the Me side chain from the nearest terminal C atom; e.g., the Me in 2-position causes a boiling point depression of 8.3°C, in the 3-position a depression of 6.4°C, etc. Each two Me side chains in α- position with respect to each other cause a 5°C rise in the boiling point.

The Stenhagens[124] of the University of Upsala, Sweden, have given solidification points for several of the CH_3 side-chain isomers of the C_{34}, C_{35} and C_{36} alkanes. These were determined in the elucidation of the structure of the methyl-substituted long-chain hydrocarbons related to *phthiocerane*, synthetically derived from phthioceric acid, a constituent of tubercle bacillus.

	Melting Points (°C)				
Hydrocarbon	Normal	2-Methyl	3-Methyl	4-Methyl	5-Methyl
$C_{34}H_{70}$	72.6	65.9	61.7	58.5	55.5
$C_{35}H_{72}$	74.4	68.0	64.0	60.6	57.9
$C_{36}H_{74}$	75.8	69.7	65.9	62.9	60.2
Phthiocerane				59.0	

At room temperature the 2-methyl-substituted compounds exist in crystalline forms in which the long chains are inclined (monoclinic or triclinic forms), while the 3-, 4-, and 5-methyl-substituted hydrocarbons at this temperature have the orthorhombic structure found in normal-chain hydrocarbons. At 10 to 15 degrees below the melting point the methyl-substituted compounds show a transition to a crystalline structure with tilted chains (monoclinic or triclinic in form) which persist up to the melting point; this behavior is not shown by the normal-chain compounds.

Cycloparaffins. Polymethylene hydrocarbons having ring structures are encountered in fossil lignite and in petroleum waxes. They are known as *naphthenes*, and have the formula C_nH_{2n} for both pentagonal and hexagonal single ring structures, with the attached polyethylene straight chain or

chains attached. The physical constants of a few of the simpler normal cycloparaffins are given below.

Cycloparaffin	M.P. (°C)	Density (d_4^{20})	Refractive Index (n_D^{25})
C_8 Cycloöctane	13.5,[125] 11.5[7]	—	1.4558 (n_D^{25})
C_9 Cyclononane	9.7[125]	0.7590	1.4214
C_{10} Cyclodecane	10.8[125]	0.7759	1.4205
C_{12} Cyclododecane	61.0[125]	0.7865	1.4307
C_{13} Cyclotridecane	23.5[125]	0.7952	1.4370
C_{26} 1-Cyclohexyleicosane	47.9[22]	—	1.4398 $(n_D^{50})^{23}$
C_{25} 1-Cyclopentylheneicosane	45.4[22]	—	1.4379 $(n_D^{50})^{23}$

1-Cyclohexyleicosane crystallizes in square and rectangular plates; 1-cyclopentylheneicosane crystallizes in hexagonal plates[22]. Refractive indices (n^{16}) have been listed as 1.4578 and 1.4328 for cycloöctane and cyclononane, respectively, by Bell[7].

Where the position of the ring is away from the end of the straight chain, the melting point is so low that the naphthene is liquid at room temperature. Unsaturated cycloparaffins are liquids, and are not generally encountered in waxes.

Crystal Types of Hydrocarbons. Crystal types of pure hydrocarbons in the paraffin wax range have been the subject of study by Clarke[22]. Twenty-three pure hydrocarbons comprising paraffinic, naphthenic, and aromatic compounds in the molecular range of paraffin wax were obtained from A.P.I. Project 42. These pure hydrocarbons were crystallized from the melt at different rates and from solutions of ethyl actate and nitrobenzene at different rates and over a wide range of temperatures. The two major factors in determining whether needles, plates, or malcrystalline masses were formed by each of the pure hydrocarbons were (1) the rate of crystallization of the solute or the melt, and (2) the temperature difference between the melting point of the pure hydrocarbon and the cloud point (or crystallizing temperature of the solution). Needle crystals could be obtained from *n*-hexacosane only by adding small percentages of resinous impurities.

Three methods were employed for crystallizing the pure hydrocarbons: (1) crystallization from solution in hanging drop slides; (2) crystallization from solution by evaporation of the solvent on glass microslides; (3) crystallization from the melt on the surface of glass microslides.

Unsaturated Hydrocarbons

Unsaturated hydrocarbons are seldom encountered in natural waxes, unless they have become overheated in melting. *Heptadecene*, $C_{17}H_{34}$, may be obtained from the pyrolysis of stearic acid. Olefins are sometimes found in marine oils, e.g., *n-octadecylene*, $C_{18}H_{36}$ (m. 17.5°C), in shark-liver oil, accompanied by *squalene*, a highly unsaturated hydrocarbon, namely

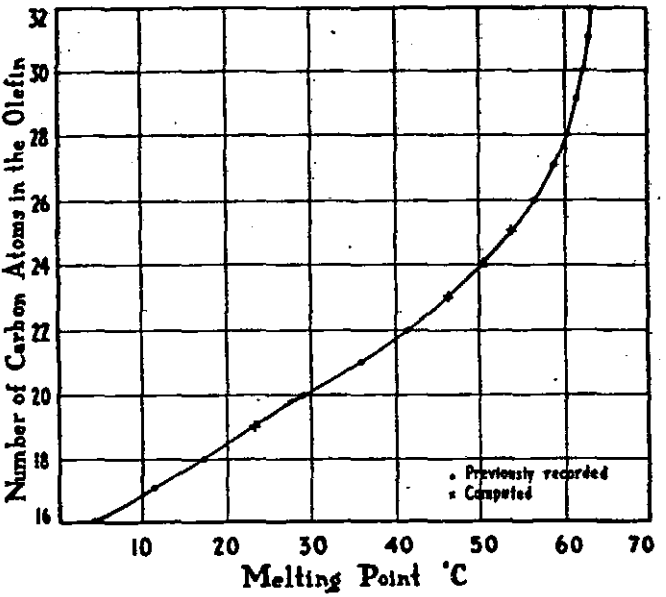


FIGURE 1. Melting points of olefins.

2, 6, 10, 15, 19, 23-hexamethyltetracosahexaene-2, 6, 10, 14, 18, 22. Olefins are seldom encountered in the paraffin waxes.

A hydrocarbon, *cerotene*, $C_{26}H_{52}$ (m. 56.5°C), has been reported as a constituent in the shell of a coccid, *Pulvinaria horii*, by Kono[72]; also in the distillate of lignite, and of Galician petroleum. This hydrocarbon may be of a cyclic polyethylene type, and not straight-chain. *Heptacosylene*, $C_{27}H_{54}$ (m. 58°C), has been obtained by the distillation of Chinese insect wax. *Melene*, $C_{30}H_{60}$ (m. 62°C), has been obtained by the distillation of beeswax, probably through the pyrolysis of a C_{31} acid. Marcusson and Böttger[94] have shown that melene (m. 62–63°C, d^{25} 0.9037, d^{65} 0.7913, n_{90} 1.4228) can be found in peat-tar paraffin (distillate with $AlCl_3$), and abundantly in Indian paraffin, from which it is obtained by fractional distillation from benzene, followed by petroleum ether. Melene is sometimes mistaken for naphthene.

Dotriacontene, $C_{32}H_{64}$ (m. 64°C), has been prepared by Pummerer and Kranz[118] from carnauba wax. From the highest alcohol (m. 87–88°C) of the wax they prepared a palmitate, which by refluxing under 13 mm pressure of CO_2 they were able to fractionate a crude unsaturated hydrocarbon which, when purified and crystallized from acetone, yielded silver-felted crystals (melting at 64°C, molecular weight in camphor 444.8, in naphthalene 466.5–492.5).

Alkenes with a double union in a different position from the normal 1-position are also encountered in waxes; for example, the C_{21} alkene, 13-

TABLE 3. STRAIGHT-CHAIN WAX OLEFINS

Olefin	C_nH_{2n}	Melting Point (°C)	Boiling Point (°C) 15 mm	1.5 mm
Cetene (1-hexadecene)	$C_{16}H_{32}$	4.0 (Messer)	155	120
1-Heptadecene	$C_{17}H_{34}$	11.0 (Schmidt)	169	127
Octadecylene (1-octadecene)	$C_{18}H_{36}$	17.5 (Niemann)[109]	179	136
1-Nonadecene	$C_{19}H_{38}$	24.0*	187	144
Eicosylene (1-eicosene)	$C_{20}H_{40}$	28.5 (Niemann)[109]	196	151
1-Heneicosene	$C_{21}H_{42}$	35.5 (Schmidt)	205	158
Docosylene (1-docosene)	$C_{22}H_{44}$	41.0 (Braun)	214	166
1-Tricosene	$C_{23}H_{46}$	46.0*	223	174
Tetracosylene (1-tetracosene)	$C_{24}H_{48}$	50.0*	233	181
1-Pentacosene	$C_{25}H_{50}$	53.5*	242	188
Cerotene (1-hexacosene)	$C_{26}H_{52}$	56.5 (Karrer)	251†	195†
Heptacosylene (1-heptacosene)	$C_{27}H_{54}$	58.5	260†	202†
Octacosylene (1-octacosene)	$C_{28}H_{56}$	60.0	269†	210†
1-Nonacosene	$C_{29}H_{58}$	61.0	277†	218†
Melene (1-triacontene)	$C_{30}H_{60}$	62.0 (Brodie)	285	225
1-Hentriacontene	$C_{31}H_{62}$	63.0 (P&K)[116]	295†	233†
1-Dotriacontene	$C_{32}H_{64}$	64.0	303	240 (P&K)[116]

* Computed melting point. †Computed boiling point.

heneicosylene (b_{12} 201–202°, m. 3°C). Alkenes have lower specific gravities than *alkanes*. At their melting points the specific gravities of C_{12}, C_{14}, C_{16} and C_{18} alkenes are 0.795, 0.794, 0.792, and 0.790, respectively. At 24°C the specific gravity of eicosylene, $C_{20}H_{40}$, is 0.8181, and its boiling point at 760 mm is 314–315°C. The specific gravity of eicosane, $C_{20}H_{42}$, is 0.9164 and its boiling point 309.7°C.

Wax Alcohols

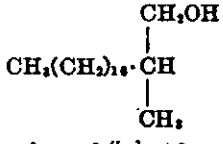
The unsaponifiable matter in waxes includes all those substances which remain insoluble in water after the wax has been totally saponified by alcoholic potassium hydroxide, or its equivalent, followed by the addition of an excess of water, and separation of the unsaponifiable by a selective solvent. The unsaponifiable consists chiefly of wax alcohols—straight-chain or cyclic in structure, or both—and hydrocarbons. Analytically, the wax alcohols are destroyed by treatment with fuming hydrochloric acid, leaving the hydrocarbons intact.

Many of the animal and vegetable waxes yield 35 to 55 per cent of fatty or wax alcohols, free and combined (as esters), whereas the fats yield only 1 to 2 per cent of fatty alcohols, since the glycerol (polyhydric alcohol) produced by the hydrolysis is water-soluble.

In listing the fatty and wax alcohols the common nomenclature is used in Table 4, although the Geneva system is also referred to. Under the rules of the International Union the final *e* of the name of a hydrocarbon becomes 'ol' for its corresponding alcohol: for example, eicosane ($C_{20}H_{42}$) and eicosanol ($C_{20}H_{42}O$). If, for example, the C_{20} alcohol is the normal one it is referred to as *arachic alcohol*, or *n*-eicosanol, the latter denoting the straight-chain alcohol, $CH_3 \cdot (CH_2)_{18} \cdot CH_2OH$.

The x-ray crystal spacings of the alcohols differ little from those of the corresponding straight-chain carboxylic acids. The chain lengths increase in regular fashion from 41.35 to 71.0 Å (B values) for the C_{18} to the C_{32} range of alcohols. The long x-ray spacing of isostearyl alcohol is 34.8 Å[135a].

Some of the monohydric alcohols, encountered in natural waxes, particularly those of 20 or more carbons, are not identical with those with an equal number of carbons produced synthetically. Often little is known or recorded of their structure and optical activity, if any. When there is a CH_3 side chain linkage, if the CH_3 group is adjacent to the CH_2OH, or primary alcohol group, the melting point will differ only slightly from the normal chain alcohol. For example,



2-methylnonadecanol ($[\alpha]_D$ 4.8, m.p. 62–63°C)

This isomer of eicosanol (m. 65.3°C) was isolated from the bacillus of timothy grass (*Phleum pratense*) by the Stenhagens[135]. These investigators were the first to observe monolayers of an optically active long-chain waxy compound.

Many of the natural isomers of the monohydric alcohols have the CH_3 group attached to the second to last carbon (C which is farthest away from the OH group); the melting point of these iso-alcohols is appreciably lower than that of the corresponding *n*-alcohol. *Carnaubyl alcohol*, the alcohol of woolwax (wool fat) was one of the first isomers of *n*-tetracosanol to be recognized as having a side-chain methyl group. The position of the CH_3 linking in carnaubyl alcohol is not definitely known; this alcohol is thought to be DL-22-methyltricosanol, or isolignoceryl alcohol. *Isoceryl alcohol* (24-methylpentacosanol) is a constituent of several natural waxes, including woolwax.

TABLE 4. SOLID NORMAL SATURATED MONOHYDRIC ALIPHATIC ALCOHOLS OF SYNTHETIC ORIGIN ($C_n H_{2n+2} O$).

C Number	Systematic Name	Common Name	M.P. (°C)	B.P. (°C) at 760	B.P. (°C) at 15	B.P. (°C) at 0.25 mm
10	*n*-Decanol	Capryl	6.9, 6.0 (f.p.)[k]	232[z]	120_{12}[y]	—
11	*n*-Hendecanol	Hendecyl	16.3[o], 15.8 (f.p.)[k]	243	131[y]	—
12	*n*-Dodecanol	Lauryl	23.8[o], 23.9 (f.p.)[k]	257[z]	150_{20}[y]	—
13	*n*-Tridecanol	Tridecyl	30.2, 30.6 (f.p.)[k]	—	155.5[y]	$117_{0.5}$[f]
14	*n*-Tetradecanol	Myristyl	37.7[m], 37.6 (f.p.)[k]	286	171.5_{30}[y]	—
15	*n*-Pentadecanol	Pentadecyl	43.9, 43.8 (f.p.)[k]	—	176	—
16	*n*-Hexadecanol	Cetyl	46.8[a], 49.1[s], 47.1[o]		190[y]	—
17	*n*-Heptadecanol	Margaryl	54.0[f], 53.3 (f.p.)[k]		—	
18	*n*-Octadecanol	Stearyl	58.8[o], 57.9 (f.p.)[k], 59[j]		210[f]	153.5[a]
				15	0.25	0.02 mm
19	*n*-Nonadecanol	Nonadecyl	62.5[a], 61.6 (f.p.)[y]	—	$166.5_{.32}$[y]	—
20	*n*-Eicosanol	Arachic	65.9[o], 65.3[j]	220_2[y]	$178_{.40}$[y]	—
21	*n*-Heneicosanol	Heneicosyl	68.5[a]	—	—	—
22	*n*-Docosanol	Behenyl	70.6[p], 70.6 (f.p.)[y]	—	$180_{.22}$[y]	—
23	*n*-Tricosanol	Tricosyl	74.0[a]	—	$192_{.70}$[y]	—
24	*n*-Tetracosanol	Lignoceryl	76.1[x], 75.4[j], 73.6 (f.p.)[v]	—	$210_{.40}$[y]	—
25	*n*-Pentacosanol	Pentacosyl	79.0[a]	—	$215_{.16}$[y]	
26	*n*-Hexacosanol	Ceryl	80.5[g], 79.5[j], 78.8 (f.p.)[y]	—	—	—
27	*n*-Heptacosanol	Heptacosyl	86.5	—	—	—
28	*n*-Octacosanol	Montanyl	84.5, 83.0[j], 82.6 (f.p.)[v]	—	—	175
29	*n*-Nonacosanol	Nonacosyl	84.1 (f.p.)[y]	—	—	—
						at 0.5 mm
30	*n*-Triacontanol	Myricyl	86.8[t], 85.1 (r.p.)[v]	—	—	244
31	*n*-Hentriacontanol	Melissyl	87.0, 85.5[c]	—	—	—
32	*n*-Dotriacontanol	Lacceryl	89.0, 89.2[h], 88.9 (r.p.)[v]	—	—	257
33	*n*-Tritriacontanol	—	88.6[h]	—	—	—
34	*n*-Tetratriacontanol	Geddyl	93.5, 91.7[b], 90.9 (r.p.)[v]	—	—	267
35	*n*-Pentatriacontanol	—	91.5[h]	—	—	—
36	*n*-Hexatriacontanol		94.5, 92.9[b], 92.6 (f.p.)[y]	—	—	—
44	*n*-Tetratetracontanol	Takakibyl	99.0	—	—	—

[a]by Levene and Taylor[83] (mean of the reported range); [b]by Francis, Collins, and Piper[36]; [c]m.p. by Heiduschka and Gareis[53]; [d]m.p. by Gascard; [e]m.p. by Verkade; [f]by Levene *et al.*[84]; [g]by Jacini[65]; [h]by Jones[67]; [i]by Adam and Dyer[1]; [j]by Bleyberg and Ulrich[10]; [k]by Meyer and Reid[101] (α form stable, α crystal freezing point corresponds to lowest melting point); [l]by Mrs. Robinson[121]; [m]setting point by Garner and Rushbrooke (1927); [n]average of 59[a, j], and 58.5[f]; [o]average of 66[a], 66.5[f], and 65.2[j]; [p]average of 71[a], 70.8[b], 70–70.4[w] and 70.3[j]; [q]average of 77[a], and 75.3[b, j]; [t]average 87.5[c], 86.6[b] and 86.5[j]; [s]46.7–47.5 by Ruzicka and Prelog; [v]resolidification point of alcohol from carnauba wax by Murray and Schoenfeld[105]; [w]m.p. by Schuette *et al.* (1948); [x]by Schon[129b] (mean of range reported); [y]as adapted by Ralston[118]; [z]by Mlle. Delcourt.[28a]

TABLE 5. ISOMERS OF THE *n*-MONOETHANOID WAX ALCOHOLS: C_nH_{2n+1}, CH_2OH

Normal Alcohol	M.P. (°C)	Isomer	M.P. (°C)
Even Number of Carbons			
C_{18} Stearyl (*n*-octadecanol) $CH_3 \cdot CH_2(CH_2)_{16}CH_2OH$	58.8	16-Methylheptadecanol CH_3 \ $CH \cdot CH_2(CH_2)_{13}CH_2OH$ / CH_3 (isostearyl)	40.1–40.3[125a]
C_{20} Arachic (*n*-eicosanol)	65.0–65.5[1], 65.5–66.5[83]	18-Methylnonadecanol-(isoeicosyl)	50.3[105]
C_{22} Behenyl (*n*-docosanol)	70.6, 71[83]	20-Methylheneicosanol (isobehenyl)	57.1[105]
C_{24} Lignoceryl (*n*-tetracosanol)	75.8, 76.5–77.5[53]	22-Methyltricosanol (isolignoceryl)	72[85], 62.4[105]
C_{26} Ceryl (*n*-hexacosanol)	79.5[19], 79[47]	24-Methylpentacosanol (isoceryl)	67.2[105]
C_{28} Montanyl (*n*-octacosanol)	83.2	26-Methylheptacosanol (isomontanyl)	72?
C_{30} Myricyl (*n*-triacontanol)	87.5[53], 88[47]	28-Methylnonacosanol (isomyricyl)	78
gossypyl forms			
α	87		
β	86		
γ	82		
C_{32} Lacceryl (*n*-dotriacontanol)	89[46], 91	30-Methylheneicontanol (isolacceryl)	81?
C_{34} Tetratriacontanyl (*n*-tetratriacontanol)	92.4	31-Methyltritriacontanol	78?
		sorbyl	78
		incarnatyl	73, 69–70[21]
Odd Number of Carbons			
C_{21} Heneicosyl (*n*-heneicosanol)	68.5[53]	D-18-Methyleicosanol (anteisoheneicosyl)	40.1[105]
C_{23} Tricosyl (*n*-tricosanol)	74.0[83]	D-20-Methyldocosanol (anteisotricosyl)	48.5[105]
		21-Methyldocosanol (isotricosyl)	69.0[84]
C_{25} Pentacosyl (*n*-pentacosanol)	79.0[83]	D-22-Methyltetracosanol (anteisopentacosyl)	54.6[105]
		23-Methyltetracosanol (isopentacosyl)	75.0[83, 84]

TABLE 5 (*continued*)

Normal Alcohol	M.P. (°C)	Isomer	M.P. (°C)
Odd Number of Carbons—*Continued*			
C_{27} Heptacosyl (*n*-heptacosanol)	82.8	D-24-Methylhexacosanol (anteisoheptacosyl)	61.0[105]
		25-Methylhexacosanol (isoheptacosyl)	78.0
		carboceryl	79, 79.5, 80.2
C_{29} Nonacosyl (*n*-nonacosanol)	83.7[67]		
C_{31} Hentriacontanyl (*n*-hentriacontanol)	87.0[46, 67]	28-Methyltriacontanol (anteisohentriacontanyl)	67.0?
		29-Methyltriacontanol (isohentriacontanyl)	73.0?
C_{33} Tritriacontanyl (*n*-tritriacontanol)	88.6	30-Methyldotriacontanol (anteisotritriacontanyl)	69.0?
		psyllostearyl	69.0

Note: D-3-methyltricosanol melts at 57.2°C (Ställberg-Stenhagen-1951).
Melting points for melissyl alcohol have been given as 85.8, 87.0, 83.5°C. Melissyl alcohol should probably be regarded as an isomer of myricyl alcohol.

It appears to be an axiom that *normal* monomeric odd-chain alcohols are not formed in nature. The normal C_5 alcohol (valeryl alcohol) does not so exist, although the iso-C_5 alcohol (isovaleryl alcohol) does play an important role in the metabolism of plants.

Recent investigations have shown that in some of the natural waxes, iso-acids (with an uneven number of carbons) accompany normal acids, and we must likewise expect iso-alcohols to accompany normal alcohols in the same manner. There are instances where the chain alcohols containing an odd number of carbons appear in reality to be equimolecular compounds of normal and iso-alcohols locked in the same crystal cell structure. The crystal structures containing both alcohols of even and odd carbons are known as *mixed dimers*. There are three recorded ceryl alcohols approaching the C_{25}, C_{26}, and C_{27} compositions. These natural odd-carbon alcohols are iso-alcohols, or at least alcohols with a methyl side-chain linkage, rather than mixtures of normal alcohol homologs having an even number of carbons. *Neoceryl alcohol* ($C_{25}H_{51}OH$) may be the equivalent of isopentacosanol, and *carboceryl alcohol* ($C_{27}H_{55}OH$) the equivalent of isoheptacosanol.

Alcohols with the methyl side linkage in the preultimate position have a

trifle lower melting point than the corresponding *n*-alcohols. Other isomers have appreciably lower melting points, and are of different rotatory power.

Secondary Alcohols. The main constituents of many of the plant waxes appear to be *n*-long-chain primary alcohols. Kreger[78], however, has discovered secondary alcohols of 31, 33, 27, and 25 carbons, one of each in four plant waxes. The secondary alcohols have been reported as *hentriacontan-16-ol, tritriacontan-17-ol, d-heptacosan-9-ol,* or *d-pentacosan-8-ol.* A secondary alcohol of 29 carbons, *d-nonacosan-10-ol* had been previously reported as a component of apple skin wax. Nonacosan-10-ol was also discovered in the growing tips of the slashpine (*Pinus caribaea* Morelot). *Nonacosan-15-ol,* $CH_3(CH_2)_{13}OH(CH_2)_{14}CH_3$, has been reported as a constituent of Brussels sprouts (*Brassica oleracea gemmifera*).

Cyclic Alcohols. A few waxes, particularly floral waxes, contain cyclic alcohols, or cyclonols. These have a saturated hexagonal ring, a CH_2OH group, and one or more alkyl groups. For example, cyclodecanol, $C_{10}H_{20}O$ (b. 125°C, m. 40–41°C) is methylethylcyclonol. Homologs include cyclodecanol (m. 80°C), cyclotetradecanol (m. 79–80°C), cyclohexanol (m. 79–80°C), cycloöctadecanol, and cycloeicosanol, $C_{20}H_{40}O$ (m. 69°C).

Natural Occurrence of Wax Alcohols. *Cetyl alcohol* ($C_{16}H_{34}O$) occurs in the combined state as cetyl palmitate in spermaceti. Cetyl alcohol (ethal) was discovered by Chevreul over a century ago. It can now be prepared cheaply from cetyl palmitate by hydrogenation, and is of considerable use in the cosmetic industry. It crystallizes from alcohol in leaflets (m. 49–50°C). *Heptadecyl alcohol* crystallizes in pearly white scales (m. 54°C). *Stearyl alcohol* occurs in montan wax and in cotton, and crystallizes from alcohol in shining leaflets (m. 58.5°C). *Arachic alcohol* ($C_{20}H_{42}O$), or eicosanol is a constituent of the lignin residue from Douglas fir, as is also *behenyl alcohol* ($C_{22}H_{46}O$). *Lignoceryl alcohol* and its isomer *carnaubyl alcohol* are constituents of waxes.. *Ceryl alcohol* occurs as ceryl cerotate in Chinese insect wax, and accompanies *myricyl alcohol,* $C_{30}H_{62}O$, in japanwax. Ceryl alcohol crystallizes in rhombic plates (m. 79.5–80°C). Myricyl alcohol and *lacceryl alcohol* ($C_{32}H_{66}O$) occur both free and combined in carnauba wax. Myricyl alcohol crystallizes from ether in needles (m. 86.5°C, Robinson). *Melissyl alcohol* ($C_{31}H_{64}O$) occurs in beeswax in the combined state as melissyl melissate. It crystallizes in white brilliant micro-lozenges (m. 87°C). It is also not unlikely that melissyl alcohol is a C_{30} alcohol.

Lacceryl alcohol in the form of lacceryl lacceroate (m. 95°C) was discovered by Gascard[46] in the wax obtained from commercial "sticklac." It crystallizes in brilliant pearl needles (m. 89°C) consisting of lozenge-shaped micro-lamellae, characteristic of the higher alcohols of this series. An alcohol resembling lacceryl has been isolated from Palaquium wax, of *P. gutta,* the gutta-percha tree. *Takakibyl alcohol,* with 44 carbon atoms, is present as a wax constituent of Koryan corn oil of Manchukuo.

Some of the wax alcohols as such have been exploited commercially, e.g., *cetyl alcohol*, which can be obtained directly from cetyl palmitate by hydrogenation. On the boundary line between waxes and oils is *lauryl alcohol* ($C_{12}H_{26}O$), which has long been available as an alcohol readily prepared by catalytic hydrogenation of its esters. A trade name for the commercial product is "Lorol." It forms a soap with sodium which can be used in somewhat acid solutions that would precipitate the fatty acids from ordinary soaps; this soap can be used in both salt and hard waters.

Heiduschka and Gareis[53] determined the melting point of carefully purified *myricyl alcohol* obtained from carnauba wax to be 87.5°C; it appears identical with the synthetic *n*-triacontanol. The next higher homolog is *n*-hentriacontanol, which has a melting point of 89.0°C. They were unable to obtain a melting point higher than 85.8°C for the alcohol isolated from beeswax, despite the fact that it was believed to be identical with *n*-hentriacontanol.

Isomers of normal alcohols with an even number of carbon atoms appear to be the more prevalent. A few of the saturated alcohols with an even number of carbons have melting points far below those of the corresponding *n*-alcohols, and are undoubtedly isomers with the methylated group ⅓ or ½ distant from the end of the chain. Examples are *carnaubyl* (C_{24}) and *incarnatyl* (C_{34}) alcohols. *Psyllostearyl alcohol* (C_{32}) has a far lower melting point than the *n*-alcohol. There appear to be at least three ceryl alcohols, the C_{25} referred to as *neoceryl*, the C_{26} both normal and isomer, and C_{27} *carboceryl*, which is an isomer of *n*-heptacosanol, which is not a constituent of natural waxes. The C_{25} alcohol is most likely a mixed dimer of lignoceryl and *n*-ceryl alcohols.

The C_{32} alcohol from carnauba wax, *dotriacontanol*, as recovered by saponification of the fractionated acetylated nonsaponifiable after chromatographing on alumina and crystallizing from petrolic ether, consists of large white laminae having a melting point of 89.2–89.4°C, and a resolidification point of 88.8°C[105]. These values correspond closely to those obtained for the synthetic C_{32} alcohol.

Crystal cell spacings (in Å) for melted layers of the alcohols are as follows: C_{14} 33.0; C_{16} 37.40; C_{18} 43.0; C_{20} 45.3; C_{21} 47.0; C_{22} 50.0; C_{24} 54.2; C_{25} 55.5; C_{26} 58.0; C_{28} 62.3; C_{30} 67.0; C_{32} 71.0. The alcohols undergo a rotational transformation at a temperature appreciably below their melting points in which the short spacings become coincident; the molecular rotation increases crystal symmetry. For example, the transformation in cetyl alcohol at 21° is rotational in character, since the spacings which near 10 are 3.8 and 4.2 Å, and become coincident above 21°.

Isomers of the saturated monohydric aliphatic alcohols have a lower melting point than the normal alcohols; e.g., D (+)-3-methyl-1-tricosanol melts at 57.2°, whereas *n*-tetracosanol melts at 75.4°C.

The specific gravities of the alcohols in the melted state are as follows:

C_{10} (d_4^{29})	0.8297[a]	C_{16}[r] (d_4^{50})	0.8197[c]	C_{24} (d_4^{77})	0.7950[b]
C_{11} (d_4^{32})	0.8334[a]	C_{17}[r] (d_4^{55})	0.8150	C_{25} (d_4^{77})	0.7890[b]
C_{12} (d_4^{34})	0.8309[a]	C_{18} (d_4^{60})	0.8124[a]	C_{26} (d_4^{85})	0.7830[b]
C_{13} (d_4^{41})	0.8277	C_{19} (d_4^{64})	0.8090	C_{30} (d_4^{88})	0.7770
C_{14} (d_4^{38})	0.8236[a]	C_{20} (d_4^{67})	0.8060		
C_{15} (d_4^{44})	0.8215	C_{22} (d_4^{72})	0.8000[b]		

[a]Listed by Ralston[118]; [b] computed value; [c] by Delcourt[28a].

Unsaturated Alcohols. Unsaturated aliphatic alcohols of the monoethylenic type are commonly associated with the liquid waxes. Most of them are liquids, but a few are solids of low melting point. The names bear the ending -eyl, -enyl, or -enol, and the hydrocarbons related thereto have the ending -ene.

Zoömaryl alcohol ($C_{16}H_{32}O$) has the constitution:

$$CH_3 \cdot CH_2 \cdot (CH_2)_3CH_2 \cdot CH{:}CH \cdot CH_2(CH_2)_4CH_2 \cdot CH_2OH$$

and is designated as *7-hexadecen-16-ol*, or *9-hexadecen-1-ol*, depending upon the terminal carbon from which the double union is counted; *11-eicosenyl alcohol*, $Me(CH_2)_7CH{:}CH \cdot (CH_2)_9CH_2OH$, would also be termed *11-eicosen-1-ol*. Unsaturated alcohols are optically right- or left-handed, that is, *cis* or *trans*; for example, *oleyl alcohol* ($C_{18}H_{35} \cdot OH$) is *cis-9-octadecen-1-ol*. Alcohols of diolefins are also encountered in the liquid waxes; for example, linoleyl alcohol $\Delta^{9:10,\ 12:13}$ which may be written *9-12-octadecen-1-dienol*.

The following is a partial list of unsaturated alcohols:

$C_9H_{17}OH$ Nonenol, a constituent of tea wax.

$C_{10}H_{19}OH$ Decenol, a liquid wax constituent of wool grease. Isodecenol (b_{18} 143–147°) is 1-decen-10-ol.

$C_{11}H_{21}OH$ Hendecenol (1-undecen-11-ol, m. −7°, $b_{4.5}$ 148.5°C), likewise is a constituent of wool grease.

$C_{12}H_{23}OH$ Dodecenol, a liquid wax, b_{11} 138–140°C, d^{15} 0.848.

$C_{14}H_{27}OH$ Physeteryl alcohol, 6-tetradecen-14-ol (iodine no. 11.2).

$C_{15}H_{29}OH$ Pentadecenol (m. 32.5°C, b_{10} 170–2°C). Isopentadecenol, 1-pentadecen-13-ol (m. 40.2°C, b_8 170°C).

$C_{16}H_{31}OH$ Zoömaryl alcohol (iodine no. 98.6), a constituent of marine oils; also palmitoleyl alcohol of beeswax.

$C_{18}H_{37}OH$ Oleyl alcohol, *cis*-9-octadecenol (b_{760} 340°, b_{15} 205–10°C), of marine oils.

$C_{20}H_{39}OH$ Eicosenol (1-eicosen-11-ol, m. 25–26°C, $b_{0.1}$ 134–6°C), of jojoba wax.

$C_{22}H_{43}OH$ Docosenol (1-docosen-13-ol), a constituent of jojoba wax; closely related is the isomer, erucyl alcohol.

$C_{24}H_{47}OH$ Carnaubenol (carnaubenyl alcohol, m. 39°C), a disputed constituent of carnauba wax.

$C_{26}H_{51}OH$ Hexacosenol (m. 42°C), of jojoba wax.

Unsaturated alcohols of low molecular weight are encountered in the leaves of plants. For example, 3-hexen-1-ol, *cis*-$CH_3 \cdot CH_2 \cdot CH_2{:}CH \cdot CH_2 \cdot$

CH_2OH, has been isolated from green-tea oil, and from Japanese peppermint oil tailings. β-octenol, $CH_3(CH_2)_3CH_2{:}CHCH_2{\cdot}CH_2OH$, is another "leaf alcohol."

Carotenoids. The color, if any, of a vegetable or animal wax is due to the presence of pigment belonging to a class of compounds known as *carotenoids*. They have the basic empirical formula $C_{40}H_{56}$, and are components of the unsaponifiable fraction of fats and waxes. The yellow pigments are called *luteins*. *Lycopene*, another carotenoid, is a red pigment. The *carotenes*, α, β, and γ, are long-chain partially unsaturated hydrocarbons having partially methylated hexagonal rings at the respective terminal ends (specifically β-ionone rings). α-Carotene is strongly dextro-rotatory ($[\alpha]_D^{20} = 34°$ in benzene), whereas β-carotene is inactive. γ-Carotene has 12 instead of 11 double bonds characteristic of the other carotenes, and usually occurs in the *trans*-form. All the carotenes melt within the range of 162 to 174°C. Carotenoids include several oxides of carotene. *Lutein*, $C_{40}H_{54}(OH)_2$, has two functional alcohol groups and combined with fatty acid occurs as a natural ester in some fats and waxes. The carotenes have iodine absorption values of 520 to 570 per cent.

Sterols. The sterols comprise one of the most interesting groups of lipides, or natural wax constituents. These products are alcohols which possess a cyclic structure of four-membered rings, of which three are hexagonal and one pentagonal. The skeletal ring structure is termed *cyclopentanophenanthrene*. Sterols have 0, 1, 2, 3, or 4 double bonds.

In nature the sterols occur free, as well as combined with fatty acids in an ester linkage. In the latter case the products are waxes. All known natural sterols have a methyl group at C_{20}. The sterols which exist in higher plant life are known as *phytosterols*, those in animal life as *zoösterols*, and in those in lower plant life (e.g., fungi) as *mycosterols*. The greater number of sterols occurring in nature have 1, 2, or 3 double bonds, and 24 to 29 carbons in the molecule. The phytosterols may be grouped as follows:

Empirical Formula	Number of Double Bonds	Type Example	Rotatory Power $[\alpha]_D^n$
$C_nH_{2n-7}(OH)$	0	Dihydrositosterol	12.7°
$C_nH_{2n-9}(OH)$	1	Sitosterol	−34.2°
$C_nH_{2n-11}(OH)$	2	Stigmasterol	−51.0°
$C_nH_{2n-13}(OH)$	3	Ergosterol*	−132.0°

* Note: Ergosterol, fucosterol and zymosterol are generally classed as *mycosterols*. Fucosterol, $C_{29}H_{47}OH$ (m. 124°C, $[\alpha]_D$ −38°) and zymosterol, $C_{27}H_{43}OH$, both have two double bonds. The specific rotation of stigmasterol has also been reported as $[\alpha]^{Chf.}$ −49°.

The zoösterols may be similarly grouped:

Empirical Formula	Number of Double Bonds	Type Example	Rotatory Power $[\alpha]_D^{\circ}$
$C_nH_{2n-7}(OH)$	0	Dihydrocholesterol	+59.1°
$C_nH_{2n-9}(OH)$	1	Cholesterol	−39.0°
$C_nH_{2n-11}(OH)$	2	Lanosterol*	+58.0°
$C_nH_{2n-13}(OH)$	3	Agnosterol*	+70.6°
$C_nH_{2n-15}(OH)$	4	Carbisterol	−44.7°

* Note: Not true sterols but triterpene alcohols. Specific rotation of −39° for cholesterol is in chloroform (Chf.) It is 29.9° in ethereal solution.

Dihydrositosterol itself has the composition $C_{29}H_{51}(OH)$, and melts at 144°C. Like other sterols without double bonds, it has dextrorotatory power, its specific rotation being $[\alpha]_D^{15}$ 12.72°. Sitosterols are generally C_{29} compounds. The C_{27} compound with one double bond is sometimes called "ordinary sitosterol" to distinguish it from the C_{29} compound commonly associated with so many plant materials. For example, the walnut has as a constituent ordinary sitosterol, $C_{27}H_{45}(OH)\cdot H_2O$) (m. 142°C, $[\alpha]_D^{14}$ −33.7°). On the other hand sugarcane has a C_{29} sitosterol, $C_{29}H_{49}OH$ (m. 137–138°C, $[\alpha]_D$ −41.8°).

The stigmasterol type of sterol ranges from C_{24} to C_{30} compositions. *Stigmasterol* itself possesses the formula $C_{29}H_{47}OH$, e.g., stigmasterol of the calabar bean (m. 170°C, $[\alpha]_D^{21}$ −45°). The mycosterol known as *ergosterol*, of rye ergot, has the formula $C_{28}H_{43}(OH)\cdot H_2O$ containing three double bonds. Ergosterol melts at 165°C, and has a specific rotation of $[\alpha]_D^{20}$ −132°.

The C_{27} dihydrocholesterol, animal in origin is 7,8-dihydrocholesterol, $C_{27}H_{47}OH$ (m. 142–145°C, $[\alpha]_D$ 28.8°). *Spongasterol*, closely allied to cholesterol of sponges (family *Haliclonidæ*) melts at 147°C, and has a specific rotation of $[\alpha]_D^{27}$ −38° (cholesteryl acetate m. 144°C, $[\alpha]_D^{27}$ −43°). It is identical with the cholesterol of mussels (m. 147°C, $[\alpha]_D^{28}$ −39.5°), but is not quite identical to the cholesterol of wool fat, which melts at 148.5°C, and has a specific rotation $[\alpha]_D^{15}$ of −29.5° in 4 per cent ethereal solution[21].

γ-Lanosterol has the composition $C_{29}H_{47}(OH)$, and has two double bonds. *Agnosterol* has three double bonds, and the formula $C_{29}H_{47}(OH)$ (m. 164°C). *Carbisterol* has four double bonds. It is found in the fat of a crustacean and has the formula $C_{29}H_{43}(OH)$. It melts at 133–135°C, and its specific rotation is $[\alpha]_D^{22.5}$ −44.7°.

Characteristics of Sterols. The sterols are insoluble in water, sparingly soluble in cold alcohol, but freely soluble in a number of organic solvents including acetone. They appear in the unsaponifiable residues of the waxes of which they sometimes constitute a significant proportion. In their original natural sources the sterols occur either in the free or combined state, often roughly in the proportion of ⅓ free to ⅔ combined, the latter as esters of the fatty acids C_8 to C_{24}, frequently C_{18}. Occasionally they occur

as phosphatides in lipoid material. The free sterols are characterized by their ability to form a crystalline additive compound with the glucoside principle *digitonin*.

Digitonin test: 50 g of melted sample are shaken hot in a separatory funnel with 20 ml of a 1 per cent solution of digitonin in 96 per cent ethanol for 15 minutes. After standing several hours the lower layer is drawn off and 50 to 100 ml of ether added; the solution is then shaken and filtered. The air-dried digitonide is ground, extracted with ether, and heated with 2 ml of acetic anhydride for 1½ hr. When cool, the acetates separate out. Phytosterol acetate separates white, but the cholesteryl acetate is brown. After two crystallizations from ethanol the melting point of the acetate is determined.

Of the animal sterols (zoösterols) the one most abundantly found in nature is *cholesterol*. It forms shiny monoclinic platelets with one mol of water of crystallization, and is optically active in chloroform and ether. The melting points of cholesteryl esters are considerably below that of the free alcohol (m. 149°C); for example, *cholesteryl caprate* melts at 93°C, *laurate* at 91°C, *myristate* at 86°C, *palmitate* at 90°C, *stearate* at 82.5°C, *lignocerate* at 89°C, *oleate* (*cis*) at 44.5°C. The esters have a lower specific rotatory power than the free alcohol, and are practically insoluble in ethanol or acetone at 20°C.

Cholesterol is an important component of lanolin. Associated with cholesterol is another sterol, 7:8-dihydrocholesterol, which can be activated to a form of vitamin D (vitamin D_3) when subjected to ultraviolet light. Deuel, Jr.[31] states that since vitamin D occurs naturally as an ester, it also should be included as a part of the group of waxes.

Cholesteryl palmitate, a constituent of woolwax, has a melting point of 90°C, and a specific rotation $[\alpha]_D^{20}$ of $-25.1°$. Isomeric forms of the zoösterols, such as isocholesterol (m. 140°C) are dextrorotatory whereas cholesterol is levorotatory. The zoösterols are common in liquid marine waxes.

In 1934 Bergmann[8] showed that a zoösterol known as *ostreasterol*, found in mollusks, yielded upon reduction *ostreastenol*, identical with sitostanol, $C_{29}H_{51}(OH)$, obtained in reducing sitosterol. This was the first time that a direct relation was established between zoösterol and phytosterols. The formula of ostreasterol is $C_{29}H_{47}(OH)$, and it is isomeric with *stigmasterol*, a phytosterol found in sugarcane. *Paracholesterol*, $C_{26}H_{43}(OH)$ (m. 134–134.5°C) is found in wheat oil.

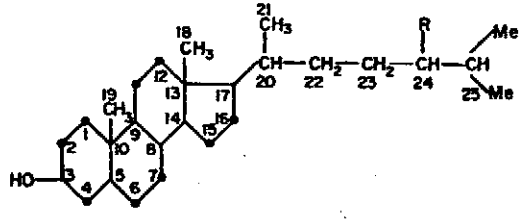
Sterols with a double unsaturated group replaced by H atoms in the chemical structure are generally referred to as *dihydrosterols*. An example of a dihydrosterol found in nature is *clionasterol* (m. 138°C, $[\alpha]_D$ −42°C), which is the *δ,6-dihydrostigmasterol* of sponges. In plant life a very high molecular weight sterol, *arisaesterol* (m. 135°C), was discovered by Marion[95] in the corms of the Indian jackinthepulpit, *Arisaema triphyllum* (L.) Schott.

It has the formula $C_{26}H_{62}(OH)_2$, and is a dihydroxysterol of type $C_nH_{2n-10}(OH)_2$. Hydroxysterols of the same type have been reported as constituents of olive leaves, namely *oleastranol*, $C_{25}H_{42}O_2$ (m. 217–218°C), and *homolestranol*, $C_{27}H_{46}O_2$ (m. 210°C). Hydroxysterols of the one double bond type, $C_nH_{2n-8}(OH)_2$ have been reported as constituents of orange peel wax, namely $C_{27}H_{48}O_2$ (m. 150°C), and $C_{26}H_{46}O_2$ (m. 139.5°C). *Betulin* (m. 251°C) of birch bark is $C_{30}H_{48}(OH)_2$ and of type $C_nH_{2n-12}(OH)_2$. It is a pentacyclic dihydric alcohol.

Sterols with 30 carbons generally prove to be triterpenes of either 5 hexagonal ring structures, namely *amyrenols*, or a 4 hexagonal-1 pentagonal ring structures, namely *lupeol*. *Taraxasterol* (of the dandelion root), $C_{30}H_{50}O$, is a pentacyclic alcohol, identifiable with the lupeol betulin group. After acetylation the taraxasteryl acetate obtained crystallizes in leaflets (m. 256–257°C, $[\alpha]_D^{18}$ 100°), which upon saponification yields needles of taraxasterol (m. 225.5–226°C, $[\alpha]_D^{20}$ 91°).

Although *ergosterol* is a plant sterol about 0.01 per cent has already been found in woolwax alcohols. Ergosterol differs from cholesterol in having two extra double bonds, one being in the side chain. Ergosterol crystallizes in monoclinic needles. It was isolated as early as 1879 by C. Tanret from the fungus ergot. It has been found to be present in some fungi as the palmitate ester. Anhydrous ergosterol melts at 163°C, and the hydrated form at 168°C.

Sterol Ring Structure. The skeletal formula given below with its cyclopentenephenanthrene ring formation, an OH identifying it as a monohydric alcohol, and an open-chain hydrocarbon residue, is common to the sterols. The number of C atoms (C_{24} to C_{31}) in the sterol varies with the length of the side chain, and the number of carbons in the R group.



● denotes CH_2 group instead of regular CH group

By replacing the single bond with a double bond in ring position 5, 6 (likewise erasing heavy dot at 6), and the epimeric R at position 24 with H, the structural formula of *cholesterol* is obtained. Replacing the single bond of cholesterol with a double bond in the 7, 8 position and providing a double bond for the 22, 23 position in the side chain, making three double bonds in all, gives *ergosterol*, a constituent of yeast. The substitution of a

double for a single bond requires the elimination of two hydrogen atoms. α-Sterol has a double bond in the 8, 14 position and β-sterol a double bond in the 14, 15 position. The *cis* and *trans* forms of sterols concern inversion of the OH and CH_3 groups from the 3 to 10 position of the carbon; the OH group in the 3 position is the *cis* compound. Cholesterol has a molecular weight of 388.64. Replacing the OH and R groups, respectively, by H gives *cholestane*, recognized as the mother substance of the sterols.

The following are examples of the sitosterols mentioned in chemical literature as having been isolated from plant material. All have the general formula $C_{29}H_{49}(OH)$.

α-Sitosterol, m. 133–138°C, $[\alpha]_D^{20}$ 13°45′ (13.75°)
α-Sitosterol,* m. 134–135°C, $[\alpha]_D$ −22.7°
β-Sitosterol, m. 139–140°C, $[\alpha]_D^{20}$ −36°11′ (36.19°)
β-Sitosterol,* m. 136–137°C, $[\alpha]_D$ −31.5°
β-Sitosterol, m. 135–135.5°C, $[\alpha]_D$ −36°
γ-Sitosterol,* m. 143–144°C, $[\alpha]_D^{20}$ −42°43′ (42.72°)
γ-Sitosterol, m. 147°C, $[\alpha]_D$ −42.8°
δ-Sitosterol,* 146–147°C, $[\alpha]_D$ −23.9°
ϵ-Sitosterol, 143–144°C, $[\alpha]_D$ −38.7°

*Sitosterols of Ichiba[64].

In ordinary α-sitosterol the double bond is in the 8, 14 position; in β-sitosterol it is in the 14, 15 position, and in γ-sitosterol it is in the 5, 6 position. For example, if the characteristics of a phytosterol are given as 142°C, $[\alpha]$ −34.2, it would be classed as ϵ-sitosterol. Variants of α-sitosterol:

α_1-Sitosterol[148], m. 164–166°C, $[\alpha]_D^{25}$ −1.7°
α_2-Sitosterol, m. 156°C, $[\alpha]_D^{25}$ 3.5°
α_3-Sitosterol, m. 142–143°C, $[\alpha]_D^{20}$ 2.5°

The α_1, and α_2-sitosterols which stem from α-sitosterol were separated by Wallis and Fernholz[148] on the basis of the relative differences in solubilities of their *m*-dinitrobenzoates. α_3-sitosterol was later isolated from the α_2-sitosterol fraction.

It is now believed that β-sitosterol and clionasterol (5, 6-dihydrostigmasterol) are "C atom 24" epimers. The same is true of stigmasterol and poriferasterol (m. 155.5 −156°C, $[\alpha]_D^{27}$ −50°.

Soybean oil foots contains β- and γ-sitosterol. β-Sitosterol (m. 136–137°C) is combined in the crude phosphatides, which on hydrolysis yield mixed sitosterols, the β-sitosterol being extracted from the alcohol-insoluble and recovered, through debromination of a sitosterol acetate dibromide.

Stigmasterol, $C_{29}H_{47}(OH)$, frequently occurs with sitosterol. It has a double bond at the 5, 6 and 22, 23 positions and an ethyl group at C_{24}. It is a constituent of rice bran, and of many of the seed oils.

Amyrins and Lupeol. α-Amyrin, β-amyrin and lupeol (m. 214°C) are not uncommon constituents of the waxes obtained from the bark, leaves, and flowers of plants. These resinols have the empirical formula ($C_{30}H_{50}O$. They have a triterpenoid structure, i.e., a skeleton of five-member rings. In the case of the amyrins all five rings are hexagonal, whereas in lupeol four are hexagonal and the fifth (E ring) pentagonal. Amyrins and lupeol have higher melting points than the sterols and are dextrorotatory. α-amyrin (α-amyrenol) crystallizes in fine, long white needles, and β-amyrenol) in long, hard needles. Their melting point and optical rotation values, formic and acetic derivatives, and eutectics (crystallized from ethanol) are given below. β-amyrin occurs in balatas in the form of its acetate.

	Melting Point °C	Rotatory Power $[\alpha]_D$ (in $CHCl_3$)
α-Amyrin	185–187[127, 24]	91.4[127], 82.3–82.8[24]
β-Amyrin	198.5[124], 197.3[24]	88.6[124], 87.8–88.4[24]
α-Amyrin formate	190	80.4
α-Amyrin acetate	225–226[127], 224–225[24]	77.9, 75.6–76[24], 83.3[127]
β-Amyrin formate	210	49.8
β-Amyrin acetate	240.5[24], 239[30]	75[30], 81.1–81.4[24]
	Eutectic Point (°C)	Percentage α-form
Mixture of amyrins	181	77.0
Mixture of amyrin formates	176	71.0

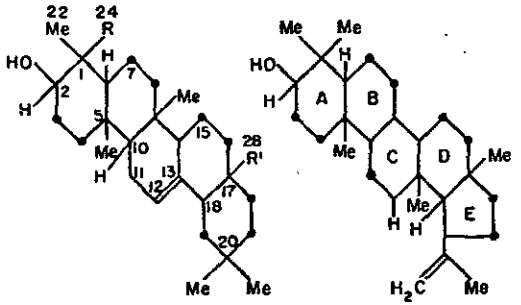
Lupeol is a principal constituent of "bresk," a concrete latex of *Alstonia venenata* of East India. This guttapercha-like substance, also known as "dead Borneo" is exported from Borneo. Lupeol is a constituent of lupine seed, gondang wax, etc. Cohen[24] described it as crystallizing in beautiful, rather long needles, and reported its constants as melting point 211°C (corrected 215°C), specific rotation ($[\alpha]_D$ in $CHCl_3$) 27.2°, acetate m. 214°C (corrected 218°C); he favors the formula $C_{31}H_{50}O$. However, the formula $C_{30}H_{50}O$ is now conceded to be correct. The structure of lupeol is similar to that of the amyrins except for the E ring, which is pentagonal. Ruzicka and Rosenkranz[126] give the melting point of lupeol as 203°C.

Another monoethylenic alcohol, germanicol, $C_{30}H_{50}O$, is found in the latex of balsam euphorbia, *Euphorbia balsamifera*, which according to David[25] differs only from β-amyrin in the position of a double bond, or perhaps in the steric configuration of a C atom. In the nomenclature of the Zürich school, it is very probably 2-hydroxy-$\Delta^{13,18}$-oleanene.

In *lupeol*, R is a methyl (Me) group, and the end group on E pentagonal ring is an isopropyl group. In *betulinol*, R is a CH_2OH group. *Betulinol*, $C_{30}H_{48}(OH)_2$ (m. 251°C), is found in large amount, over 10 per cent, in the outer bark of the birch, *Betula lenta*, whereas the amyrins occur only as a small fraction of 1 per cent in the same bark.

The triterpenoid skeletal formula for α-amyrin, and the perhydrocyclo-

pentanechrysene skeleton for lupeol are given below. Meisels, Jeger and Ruzicka[99] attempted to show that α-amyrin has methyl groups at both the 19 and 20 positions in the E ring, whereas β-amyrin has two Me (gemini-twins) in the 17 position. Tschesche and Fugmann[144a] more recently have shown in their elucidation of the structure of the dihydroxy-ursan acid, *crategolic*, $C_{30}H_{50}O_2$ (m. 254–255°C), that α-amyrin is now formulated with a geminal arrangement of 2 Me groups at C atom 20, as in β-amyrin, and a $\Delta^{13,18}$ instead of a $\Delta^{12,13}$ double bond. Sapogenins like *oleanolic acid* (m. 310°C) have a carboxyl group at C 28.



β-amyrin (m. 185–187°C) lupeol (m. 211°C, corr. 215°C)

Note: R′ = Methyl in β-amyrin R = Methyl
R′ = CH_2OH in uvaol R = Methyl
R′ = CO_2H in β-ursolic acid R = Methyl
R′ = Methyl in β-boswellic acid R = CO_2H
R′ = CO_2H in crategolic acid R = Methyl, but double bond is in the 13–17 position and there is a secondary OH at carbon 19.
● = saturated C or CH_2

Saturated Fatty and Wax Acids

The fatty acids as a class have structures likened to those of the aliphatic hydrocarbons except that a terminal CH_3 group is replaced by a carboxyl (COOH) group. They are divided into *saturated* and *unsaturated monocarboxylic acid* series, according to whether double bonds are absent or present in their hydrocarbon chains. The saturated acids, when they contain no side linkages, are known as *normal straight-chain* acids, or *n*-carboxylic acids. Saturated monocarboxylic acids are also referred to as monoethanoid acids, and the unsaturated acids as monoethenoid acids. When a CH_3 group adjoins or branches at the existing terminal CH_3 group, the acid is referred to as an iso-acid. The systematic formula for the monoethanoid series inclusive of alkyl side chain linkages is $C_nH_{2n}O_2$. The unsaturated acids with one double union of carbons in the chain have the empirical formula $C_nH_{2n-2}O_2$. The dibasic straight-chain acids have two COOH groups with the systematic formula of $C_nH_{2n-2}O_4$; they are also

called *dicarboxylic acids*. The hydroxy (OH) monocarboxylic acids have the empirical formula $C_nH_{2n}O_3$.

The boiling points of the fatty acids increase as the length of the methylene [$(CH_2)_n$] chain increases. The first member of the straight-chain series which is firmly solid is *capric acid*, ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$ COOH), which has a melting point of 31.3°C (Deffet)[28]. *Capric* (*n*-decanoic) *acid* is a constituent of coconut, palm kernel, and various seed oils. It is widely distributed in nature. The C_9 acid is *pelargonic* (*n*-nonanoic) *acid* (m. 12.3°C)[112]. At room temperature it is a liquid with a very strongly rancid odor. It is formed by the oxidative cleavage of oleic acid.

The C_{11} acid, *undecylic* (hendecanoic) *acid* (m. 28.5°C)[74] was at one time known as *umbellulic acid*, and is rarely found in nature. *Lauric acid*, $C_{12}H_{24}O_2$ (m. 44°C)[113], was first isolated from laurel kernel oil. About 50 per cent of the component acids in coconut oil is lauric acid. It is a minor constituent of some marine oils. The C_{13} acid is not present in natural fats or waxes.

Myristic acid, $C_{14}H_{28}O_2$ (m. 54.4°C)[29, 121], is an odorless, crystalline acid, and is the first of the fatty acid series to have a characteristically waxy feel. It constitutes the principal acid of the vegetable tallows such as ucuhuba fat, and the fat of the nutmeg. It is also an ordinary constituent of depot fats, marine oils, and marine algae. Isomyristic acid melts at 50.7°C.

Palmitic acid (*n*-hexadecanoic acid, m. 62.6°C)[113], is a waxy solid which is soluble in hot ethanol, like myristic acid; on cooling it crystallizes from solution in fine needles, and in pearly scales when extremely pure. Palmitic acid occurs more abundantly in nature than any of the other acids of the monoethanoid series; it was first isolated from palm oil. Isopalmitic acid (m. 62.1°C), which is pentadecanoic acid with a CH_3 side-chain linking at the end opposite to the COOH group, is a constituent of certain egg oils and of wool wax.

Margaric acid, $C_{17}H_{34}O_2$ (m. 61.3°C)[29, 121], can be synthesized, but its existence in natural fats and oils is now doubted. The term was first employed by Chevreul in 1816 to describe an acid isolated from depot fat, but which later proved to be a mixture of palmitic and stearic acids. *Daturic acid*, $C_{17}H_{34}O_2$ (m. 54.5–55.5°C)[54, 113], is reported as a constituent of certain seed fats. Its low melting point indicates that it is isomargaric acid (15-methylhexadecanoic acid). Daturic acid from the seed of jimsonweed datura (*Datura stramonium* L.), is believed to be a mixture of C_{16} and C_{18} acids, with a little C_{24} acid. An equimolar mixture of C_{16} and C_{18} acid melts at 57.5°C.

Stearic acid (*n*-octadecanoic acid, m. 69.6°C)[29, 45] was discovered by Chevreul in 1816 as one of the constituents of mutton tallow. It is widely

TABLE 6. SOLID STRAIGHT-CHAIN SATURATED FATTY AND WAX ACIDS

$C_nH_{2n}O_2$, or $C_{n-1}H_{2n-1}COOH$ (of synthetic origin)

Carbon No.	Geneva Name	Common Name	Melting Point (°C)
10	*n*-Decanoic	Capric	31.4[s], 31.3[v], 30.7[ee], 30.92[ff]
11	*n*-Undecanoic	Hendecylic	28.5[f], 30[u], 28.2[dd], 28.13[ff]
12	*n*-Dodecanoic	Lauric	43.86[ff], 44.2[t], 43.2[v]
13	*n*-Tridecanoic	Tridecylic	40.5, 41.75[dd], [ff]
14	*n*-Tetradecanoic	Myristic	54.4[d], 53.9[t], [v], 53.78[ff]
15	*n*-Pentadecanoic	Pentadecylic	52.1[b], 52.4[dd], 52.49[ff]
16	*n*-Hexadecanoic	Palmitic	62.85, [w] 62.8–63.0[v], [x] 62.41[ff], 62.9[d]
17	*n*-Heptadecanoic	Margaric	61.3[d], 60.84[dd], 60.94[ff], 59.1[hh]
18	*n*-Octadecanoic	Stearic	69.9[i], 69.5[v], 69.6[d], 69.2[ff]
19	*n*-Nonadecanoic	Nonadecylic	68.65[d], 69.5[k], 68.16[dd]
20	*n*-Eicosanoic	Arachidic	76.2[b], 77[m], 75.3[d], [o]
21	*n*-Heneicosanoic	Medullic	75.2[b], 74.3[d], 73–74[v], [dd]
22	*n*-Docosanoic	Behenic	80.5[b], 81.5[k], 79.95[d], 79.75[ss]
23	*n*-Tricosanoic	Tricosoic	78.1[dd], 79.1[d], 76.5–77.5[hh]
24	*n*-Tetracosanoic	Lignoceric	84.7[b], 81.5[k], 85[l], 84.15[d], 83[ss]
25	*n*-Pentacosanoic	Pentacosoic	84.5[k], 83.5[d], 82.45[dd]
26	*n*-Hexacosanoic	Cerotic	87.8[b], 88.5[k], 87.7[d]
27	*n*-Heptacosanoic	Heptacosoic	87.5–87.7[s]
28	*n*-Octacosanoic	Montanic	90.4[b], 90.0[t], 90.9[d], 90.2[hh]
29	*n*-Nonacosanoic	Nonacosoic	90.3[d], [i]
30	*n*-Triacontanoic	*n*-Melissic	92[b], 93.5–94[c], 93–93.2[s], 93.6[d], [i]
31	*n*-Hentriacontanoic	Hentriacontanic	93.0–93.2[s]
32	*n*-Dotriacontanoic	Lacceroic	96.0[d], 96.2[s]
33	*n*-Tritriacontanoic	Ceromelissic	94–95[p]
34	*n*-Tetratriacontanoic	Geddic	98.2[d], [aa] 98.4[s], 97.8[o], 94.8[r]
35	*n*-Pentatriacontanoic	Ceroplastic	98.4[s], 92.0[s]
36	*n*-Hexatriacontanoic	Hexatriacontanic	99.9[d], [t], 99.8[ss]
38	*n*-Octatriacontanoic	Octatriacontanic	101.6[d], [t]
40	*n*-Tetracontanoic	Tetracontanic	103.5
46	*n*-Hexatetracontanoic	Hexatetracontanic	107.1[t], 106.85[d]
56	*n*-Hexapentacontanoic	Hexapentacontanic	109.3–109.6[ee]

[b]m.p. [c](mean) by Bleyberg and Ulrich[16]; [d]m.p. by the Robinsons[120]; [e]m.p. by Francis and Piper[21]; [f]m.p. by Krafft (1883)[75]; [g]by Krafft (1878); [h]m.p. by Piper, Chibnall and Williams[112a]; [i]by Francis, Piper and Malkin[41]; [j]by Francis, Collins and Piper[38]; [k]m.p. by Gascard[45]; [l]m.p. mean of Levene and Taylor[84]; [m]m.p. by Brigl[14]; [n]m.p. by Levene *et al.*[86]; [o]b.p. by Deffet[28]; [p]m.p. by Adam and Dyer[1]; [q]listed by Ralston, p. 387, "Fatty Acids and their Derivatives"[118]; [r]m.p. by Pool and Ralston[119]; [s]m.p. by Lipp and Kovács, natural source[80]; [t]b.p. by Monick[102]; [u]listed by Markley, p. 114, "Fatty Acids"[96]; [v]m.p. by Chuit *et al.* (1927)[21]; [w]m.p. by Deffet[28]; [x]m.p. by Schuette *et al.* (1948); [y]resolid. p. by Schuette *et al.* (1948); [z]by O'Connor *et al.* (1951)[111]; [aa]by Power and Tutin (1908); [bb]by Francis, King, and Willis (1937)[40]; [cc]by Taylor and Levene[141]; [dd]by Komori and Ueno[71]; [ee]solid. p. Schuette *et al.* (1951)[130a]; [ff]m.p. by Bowman and Mason (1951); [gg]freezing points by Ralston and Hoerr[122a]; [hh]mean of Schneider and Spielman (1942)[119a]; [ii]mean of Bergmann and Swift (1951)[8a].

distributed in nature, but less widely and in smaller proportions than palmitic acid. Stearic acid can be obtained from any of the glycerides in which it occurs, but it is difficult to separate it completely from the accompanying palmitic acid. It can be prepared by hydrogen reduction of pure oleic acid. Stearic acid may also be prepared in a pure state by sulfonating a very high-grade commercial product and water-washing to remove unsaturated impurities. The saturated fatty acid fraction is esterified with methanol and fractionally distilled, the methyl stearate converted to stearic acid, repeatedly crystallized from acetone and dried over phosphorus pentoxide.

Stearic acid, when purified (f.p. 69.2°C, m.p. 69.5°C) and slowly crystallized from benzene at room temperature, yields transparent monoclinic crystals which exhibit an x-ray diffraction pattern (long spacing) corresponding to the B form of the acid. The irreversible transition of stearic acid from the B to the C form is rapid and visible at 52.9°C, but also occurs at 35.2°C when sufficient time is allowed. Crystallization of stearic acid from hot glacial acetic acid results in a product exhibiting an x-ray diffraction pattern (shorter spacing) corresponding to the C form of the acid.[132] The absolute density is 0.8474 g/ml at 72°C. The heat of fusion of stearic acid is 57.5 cal/g. Singleton and co-workers give the absolute[132] melting point as 342.83°K.

The C_{19} branched-chain acid *15-methylstearic*, when pure, melts at 40.7–42.5°C immediately after crystallization, but after standing two days or longer melts at 41.0–43.5°C[17b]; *11 methylstearic* melts at 26.2°C, but crystals separating from the melt have a lower melting point, namely 21°C[18].

Arachidic acid, $C_{20}H_{40}O_2$, crystallizes in lustrous scales which melt at 76.2°C[10]. The density (d^{77}_4) of arachidic acid when melted is 0.8375. The synthetic acid melts at 76.5°C.

Behenic acid (*n*-docosanoic acid), $C_{22}H_{44}O_2$, crystallizes in colorless needles which melt at 78.25°C[39].

Lignoceric acid, $C_{24}H_{48}O_2$, crystallizes in colorless needles from alcohol and melts at 84.15°C[39] and at 85.7°C[41] when prepared synthetically. Lignoceric acid isolated in its pure state from peanut oil melts at 80–81°C and solidifies at 77°C[141]. The synthetic acid is usually referred to as *n*-lignoceric or *n*-tetracosanoic acid. Isolignoceric acid melts at 83°C. *Carnaubic acid*, considered a C_{24} acid with methyl side chain linkage (position unknown), and found in plant material, melts at 72.5°C[118].

Hyenic acid, $C_{25}H_{50}O_2$, melts at 77–78°C. Since *n*-pentacosanoic acid melts at 83°C, hyenic acid is possibly isopentacosanoic acid which has a melting point of 78.5°C. The C_{25} acid, *14-methyltetracosanoic* when pure crystallizes from ligroin and then from acetone in very fine needles or blades which melt at 57.9–58.5°C[17b].

Cerotic acid, $C_{26}H_{52}O_2$, crystallizes in micro needles from alcohol, and melts at 86.5–87.7°C[106]. The synthetic acid melts at 88–89°C.

Carbocerotic acid, $C_{27}H_{54}O_2$, also referred to as carboceric acid (c), crystallizes from ethyl acetate or petrolic ether in needles, which melt at 82°C. The synthetic C_{27} acid, *n*-heptacosanoic, melts at 88-89°C. It is therefore not unlikely that carbocerotic is identical to isoheptacosanoic acid, which has a melting point of 82°C.

Lacceroic acid, $C_{32}H_{64}O_2$, crystallizes from benzene in lozenges, which melt at 95–96°C. The natural acid $C_{33}H_{66}O_2$ has been reported as *psyllic acid* (m. 94°C), and in all probability is isotriacontanoic acid.

Geddic acid, $C_{34}H_{68}O_2$, crystallizes from ethyl acetate as a mossy aggregate of needles, which melt at 94.5–95°C, as determined by Lipp and Casimer (1919)[91].

Most of the synthetic higher aliphatic acids, or wax acids and their derivatives, when pure, assume the form of lozenge-shaped microplates whose small diagonals divide them into two equilateral triangles.

The iso-acids manifest themselves in several optical forms, namely D(+), L(+), and L(-); e.g., *3*-methyltetracosanoic acid, $C_{25}H_{50}O_2$ has the following characteristics[134a]:

	Melting Point	Long Crystal Spacing	Specific Rotation $[\alpha]_D^{25}$	Molecular Rotation R_D^{25}
DL	68.4–68.6°C	34.2 Å	—	—
D (dextro)	65.4–65.6°C	33.0	3.46°	13.2°
D (levo)	65.4–65.6°C	33.0	−3.46°	−13.2°

Hydroxypalmitic acid, $C_{16}H_{32}O_3$, crystallizes as lustrous aggregate of needles (m. 71–72°C) from petroleum ether, or leaves by rapid evaporation of solvent. Its calcium salt (m. 134–144°C) crystallizes from alcohol in the form of warts.

Montanic acid, $C_{28}H_{56}O_2$, crystallizes in silky scales, which melt at 86°C; the acid when synthesized melts at 90.3–90.5°C.

Melissic acid (myricinic acid), $C_{30}H_{60}O_2$, crystallizes in silky scales, which melt at 90°C. The synthetic acid (C_{30}) is often referred to as *n*-melissic acid (m. 91.9–92.1°C), since many investigators have considered the natural melissic acid has the formula $C_{31}H_{62}O_2$, and crystallizes in needles (m. 90°C) from alcohol, or in rhombic plates (lozenges) from benzene. The true C_{31} acid synthetically prepared melts at 93–93.2°C. The iso-C_{31} acid melts at 90°C.

Unit Cell Crystal Structure of Wax Acids. The crystal cells of such acids as myristic, palmitic, stearic, etc., are monoclinic prismatic, and contain four molecules, which have been considered as hybrids of dimers, in which there are resonating hydrogen bonds. The hybrids are attached by

the CO linkage of the COOH groups. The long hybrid cells are bundled, and at the end appear to have an elliptical cross-section. The length of the dimer of palmitic acid is 39.10×10^{-8} cm (39.10 Å), or double that of the molecule, 19.60 Å; the first measurement is from x-ray observation, and the second by surface tension measurements made by Langmuir[79]. The bond between the CH_2 linkages is 1.21 Å in length, and shortens slightly for higher acids in the series.

The full dimensions of the crystal cell (4 molecules) of stearic acid as given by Alex Müller[104] are $a = 5.546$, $b = 7.381$, $c = 48.84$ Å, $\beta = 63.38°$. The latter is the angle that the c axis is inclined from the basal plane. Crystals of Müller's stearic acid represent a recrystallization of the pure acid from carbon disulfide.

In the liquid state there is evidence, according to Waentig and Pescheck[147], that these acids are similarly associated in double molecules or compounds. For example, when myristic acid (C_{14}) is associated with palmitic acid (C_{16}), we may have the equal molar system C_{14}—C_{16}, plus a certain amount of either C_{14} or C_{16}, according to which happens to be in excess. In the solid state the crystal cell contains pairs of dimers, which makes it possible to have the systems C_{14}—C_{16}. This is about 50 mol per cent of both C_{14} and C_{16}; C_{14}—C_{14}·C_{16}—C_{16} if about 75 mole per cent of C_{14}.

Schuette and Vogel[130] have prepared solidification point diagrams of "even" fatty acids from 8 to 36 carbon atoms. The general characteristics of all the curves studied are two breaks, one of which is near the 48 mol per cent and the other near the 73 mol per cent of the acid of lower molecular weight.

In the vapor state the behavior of the acids is monomeric, making it possible to separate them by molecular distillation, generally speaking through their alkyl esters. Whether liquid esters are monomeric or form double molecules in binary systems is still debatable; nevertheless they are separable through molecular distillation without great difficulty.

When one monocarboxylic acid is mixed with another, the melting point of the mixture is lower than that of the lower-melting constituent. For example, C_{14} acid melts at 48.3°C and C_{15} acid at 51.4°C; but the mixture of unimolar weights of these two acids melts at 42.6°C. The differential is symbolized in the literature as Δ m.p.; in the case of lower acid mixtures of C_n with C_{n+1} acids, this value is about 3 to 6°C, when the lower-melting acid has an even number of carbons; there is little or no differential when the lower-melting acid has an odd number. The Δ m.p. for mixtures of C_n with C_{n+2} acids is about 4 to 6°C, when the lower-melting acid has an even number of carbons; it is 2.5 to 5°C when the lower-melting or lower homolog acid has an odd number of carbons. For example, C_{18} and C_{20} is

70.1°C m.p., and C_{20} is 75.1°C m.p.; the mixture of C_{18} and C_{20} in unimolar weights actually melts at 64.6°C, on Δ m.p. is 5.5°C. However, for C_{19} and C_{21} it is only 2.5°C.

Acid		M.P. (°C)	C Spacing (x-ray) *d*-
Palmitic	C_{16}	62.85	35.60
Margaric	C_{17}	61.30	36.90
Stearic	C_{18}	69.90	39.75
Mixed dimer	C_{16}, C_{18}	57.90	38.80

The equimolar copolymer of palmitic and stearic has a somewhat higher *d*- (long axis) than *n*-margaric acid, but a much lower melting point.

The following are the interplanar x-ray spacings of the solid fat and wax acids. B spacings are for crystals from a nonpolar solvent, and C for the melts. Figures are in Angstrom units (Å) 10^{-8} cm, for d_1 crystal spacings[39].

	N-Acids	B (Å)	C(Å)
C_{16}	Palmitic	39.1	35.6
C_{17}	Margaric	40.4	36.9*
C_{18}	Stearic	43.7	39.7, 39.0*
C_{19}	Nonadecylic	—	40.8
C_{20}	Arachidic	48.4	44.3*
C_{21}	Medullic	49.2	45.0*
C_{22}	Behenic	52.9	48.3*
C_{23}	Tricosoic	53.4	50.3*
C_{24}	*n*-Lignoceric	57.7	52.6
C_{25}	Pentacosoic	—	53.5
C_{26}	Cerotic	62.2	56.6†
C_{28}	Montanic	67.1	61.0
C_{30}	*n*-Melissic	71.4, 71.8	65.7, 65.1
C_{32}	Laceroic	76.3	69.2
C_{34}	Geddic	80.5	73.3
C_{36}	Hexatriacontanoic	85.2	78.1
C_{38}	Octatriacontanoic	90.0	82.1
C_{46}	Hexatetracontanoic	108.2	99.0
C_{16}, C_{18}	Bimolecular compound	—	38.85*

* (Francis, Collins, and Piper).
† Morgan & Holmes.

Markley[96] states that freezing point data are preferable for the construction of temperature curves, and gives the following f.p. (°C) values for the *n*-monoethanoid acids: C_{10} 31.2, C_{11} 28.1, C_{12} 43.9, C_{13} 41.8, C_{14} 54.1, C_{15} 52.5, C_{16} 62.8, C_{17} 60.9, C_{18} 69.3, C_{19} 68.8, C_{20} 74.9, C_{21} 73.7, C_{22} 79.7[39], C_{23} 78.7, C_{24} 83.9[39], C_{25} 82.9, C_{26} 97.4[39], C_{28} 90.4, C_{29} 89.7, C_{30} 93.2, C_{32} 95.5, C_{34} 98.0[39], C_{36} 99.7[39], C_{38} 101.5.

TABLE 7. BOILING POINTS OF *n*-CHAIN ACIDS OF HIGHER MOLECULAR WEIGHT

Carbon No.	B.P. (°C) at Pressure of 760	100	16	4	1 mm
10	268.7[a]	200.0[p]	159.5[q]	132.7[q]	110.3[q]
11	284.0[q]	212.5[p]	170.8[q]	143.3[q]	119.8[q]
12	298.9[q]	225.0[p]	181.8[q]	154.0[q]	130.2[q]
13	312.4[q]	236.0[p]	192.2[q]	164.2[q]	139.9[q]
14	326.4[q]	250.5[p]	202.4[q]	174.0[q]	149.2[q]
15	339.1[q]	257.0[p]	212.0[q]	182.8[q]	157.8[q]
16	351.5[q]	268.0[p]	221.5[q]	192.0[q]	167.4[q]
17	363.8[q]	277.0	230.7[q]	200.8[q]	175.1
18	376.1[q]	291.0[p]	240.0[q]	210.0[q]	183.6
19	—	297.5	246.0	—	—
20	398.0	—	—	—	204.0
22	—	306.0_{98}[p]	265.0_{15}[s]	—	—
24	—	—	272.0_{10}[r]	—	—

Note: B.p. of stearic acid at 0.25 mm pressure is 159°C; [a]b.p. by Deffet[28]; [p]listed by Ralston (1948)[112]; [q]b.p. by Pool and Ralston (1942)[112]; [r]by Mattil (1944); [s]by Monick *et al.*[102].

TABLE 8. DENSITIES (d_4^t) OF SATURATED FATTY ACIDS

	15°C	25°C	30°C	35°C	40°C	
C_{10}	1.0266[a] (solid)	1.0176[a] (solid)	0.8953 (@ 31.4° m.p.)	0.8884[a]	0.8876[a]	0.8858[a]
C_{12}	—	—	—	1.0099[a] (solid)	1.0055[a] (solid)	0.8769 (@ 43.8° m.p.)
C_{18}	0.9452 (solid)	0.9325 (solid)	—	—	0.9150 (solid)	

	50°C	60°C	70°C	80°C	90°C	100°C
C_{10}	0.8773[a]	—	0.8610	0.8531[b]	0.8452	
C_{12}	0.8707[a]	—	0.8548[a]	0.8477[b]	0.8391	
C_{14}	0.8622[a] (@ 54.4°, m.p.)	0.8580[d]	0.8528[a]	0.8439[b]	0.8365	
C_{16}	—	0.8527 (@ 62.8° m.p.)	0.8487[a]	0.8414[b]	0.8347[a]	
C_{18}	—	0.8900 (solid)	0.8479	0.8386[b]	0.8335	
C_{20}	—	—	—	—	—	0.8240[e]

The densities (d_b^{100}) of C_{22}, C_{24}, C_{26}, and C_{28} acids are 0.8221, 0.8207, 0.8198 and 0.8191, respectively, as given by Bleyberg and Ulrich[e]. See Table 9.

[a] Garner and Ryder[42]; [b]Dorinson, McCorkle and Ralston[29]; [d]listed by Ralston[112]; [d]listed by Markley[96]; [e]by Bleyberg and Ulrich[19]; [f]by Holde and Gentner[59].

TABLE 9. ISOMERS OF THE HIGHER MONOETHANOID ACIDS

N-Acid	Formula	M.P. (°C)	Isomer	M.P. (°C)
Lauric	$C_{12}H_{24}O_2$	43.7[qq]	10-Methylhendecanoic (isolauric)[a]	41.2[iii]
Tridecylic	$C_{13}H_{26}O_2$	40.5[dd]	D(+)-2-Methyllauric	21.2–22[vv]
			DL-2-Methyllauric	24[vv]
			10-Methyllauric	6.2, 5.6
			11-Methyllauric (isotridecylic)	41[fff]
Myristic	$C_{14}H_{28}O_2$	53.7[aaa], 54.9[oo]	2-Methyltridecanoic	27 ?
			12-Methyltridecanoic (isomyristic)	53.3[a, fff] 50.8[e, yyy]
Pentadecylic	$C_{15}H_{30}O_2$	50.5[mm], 51	2-Methylmyristic	34–36[ooo]
			12-Methylmyristic (anteisopentadecylic)	23
			13-Methylmyristic (isopentadecylic)	51.75[fff]
Palmitic	$C_{16}H_{32}O_2$	62.6[d], 63[oo]	2-Methylpentadecanoic	48[qqq]
			5-Methylpentadecanoic	52.9
			14-Methylpentadecanoic[a] (isopalmitic)	61.5[fff], 62.4[a], 57.5[e], 62.1[e]
Margaric	$C_{17}H_{34}O_2$	58.5[mm], 61.3	2-Methylpalmitic[a]	54[qqq]
			3-Methylpalmitic	41[www]
			14-Methylpalmitic (anteisomargaric)	36.8[ii], 37.2, 39.8
			15-Methylpalmitic (daturic[f, s], isomargaric)	55.0, 59.6[ff]
Stearic	$C_{18}H_{36}O_2$	69.4[s], 69.8[oo]	2-Methylheptadecanoic	51–51.5[qqq]
			14-Methylheptadecanoic	42.7–43[vv]
			15-Methylheptadecanoic (anteisostearic)	43.6[aaa]
			16-Methylheptadecanoic (isostearic)	69.5[a], 67.9[e] 67.8–68.5[rrr]
Nonadecylic	$C_{19}H_{38}O_2$	68.8[dd], 67[www]	2-Methylstearic	54.9[ii], 54[zz], 58[qqq], 54.5[xxx]
			3-Methylstearic	51.0[ii], 49[zz]
			4-Methylstearic	52.7[ii], 50.5[zz]
			5-Methylstearic	44.8[bbb]
			6-Methylstearic	40.3[bbb]
			7-Methylstearic	37.1[bbb]
			8-Methylstearic	34.3[bbb]
			DL-9-Methylstearic	38.8[bbb, nnn]
			DL-10-Methylstearic	25.8[ii], 24–25[vvv]
			D(+)-10-Methylstearic	13–13.5[ii]
			L(−)-10-Methylstearic (tuberculostearic)	12.8–13.4[ii], 10–11[bbb]
			DL-11-Methylstearic	32.9[nnn]
			D-11-Methylstearic	19.8[nnn]

TABLE 9 (*Continued*)

N-Acid	Formula	M.P. (°C)	Isomer	M.P. (°C)
Nonadecylic —*continued*	$C_{19}H_{38}O_2$	68.8[dd], 67[vvv]	L-11-Methylstearic	20.0[nnn]
			12-Methylstearic	36.9[bbb]
			13-Methylstearic	30.5[bbb]
			14-Methylstearic	36.4[vv], 37.4[bbb]
			15-Methylstearic	41.6[ttt], 42.3[bbb]
			16-Methylstearic (anteisononadecylic)	46.8[hh], 50.3[kk]
			17-Methylstearic (isononadecylic)	67.3–67.8[zz]
Arachidic	$C_{20}H_{40}O_2$	76.5[ee], 75[kkk]	2-Methylnonadecylic	57
			3-Methylnonadecylic	48[ss]
			DL-11-Methylnonadecylic	33[jjj], 32.9[nnn]
			D(+)-11-Methylnonadecylic	19.7–20[nnn]
			L(−)-11-Methylnonadecylic	19.9–20.1[nnn]
			18-Methylnonadecylic (isoarachidic)	75.3[iii]
Medullic	$C_{21}H_{42}O_2$	75.5[oo]	2-Methyleicosanoic	61.7–62[hhh], 61.7[xxx]
			18-Methyleicosanoic (lanoarachidic)	55.6, 55.8, 57.4
Behenic	$C_{22}H_{44}O_2$	81.5[oo], 79.9[kkk]	2-Methylheneicosenoic	63[uu]
			20-Methylheneicosanoic (isobehenic)	79.4[iii], 75[rr]
			Isobehenic	75.5[i], 76.5[j], 69.5[ee]
Tricosanoic	$C_{23}H_{46}O_2$	78.9[vv], 80.5[oo]	2-Methyldocosanoic	66.8[ii], 67.2[hhh] 68.5[w], 67.3[xxx]
			10-Methyldocosanoic	45.5–46[hhh, aaa]
			20-Methyldocosanoic[a]	62.1
			21-Methyldocosanoic (isotricosanoic)	77.0[ff], 73.5[uuu]
n-Lignoceric	$C_{24}H_{48}O_2$	84[vv], 85.5[oo], 84.1[kkk] 85.5–86[rr]	DL-2-Methyltricosanoic (3 m.pts.) m. 68–68.5 (vitreous), plates 70.2, and 74.	
			D-3-Methyltricosanoic	62.2[ddd]
			Carnaubic	72.5, 72[m], 73.5[k]
			20-Methyltricosanoic	79.4[ii]
			D(−)-21-Methyltricosanoic	67.8–68.1[ggg]
			22-Methyltricosanoic (isolignoceric)	83.1[ii], 83.3[ff]
			Lignoceric (natural)	80.5[ff], 81[eee]
Pentacosanoic	$C_{25}H_{50}O_2$	82.6–83.2[jj]	2-Methyltetracosanoic	72.3[xxx], 72[mmm]
			D(+)-3-Methyltetracosanoic	68.6[iii]

TABLE 9. (*Continued*)

N-Acid	Formula	M.P. (°C)	Isomer	M.P. (°C)
Pentacosanoic—*continued*	$C_{25}H_{50}O_2$	84.5	D(+)-4-Methyltetracosanoic	63.8[ddd]
			6-Methyltetracosanoic	55.8–56.6[kk]
			10-Methyltetracosanoic	50–51[ff], 51.0–51.5[xxx]
			12-Methyltetracosanoic	43.8–44.6[vv]
			14-Methyltetracosanoic	58.2[ff, ttt]
			18-Methyltetracosanoic	55.7
			21-Methyltetracosanoic	60.7[ss]
			22-Methyltetracosanoic (anteisopentacosanoic)[a]	62.1, 68.1
			23-Methyltetracosanoic (hyenic, neocerotic)	78.5[a, uuu], 81, 82.5[fff] 77.8[o, q, ww, eee]
n-Cerotic	$C_{26}H_{52}O_2$	87.7[tt], 88.5[oo], 87.6[kkk]	5-Methylpentacosanoic	52.9[ddd]
			10-Methylpentacosanoic	54–55[aaa]
			21-Methylpentacosanoic	56.6[ss]
			24-Methylpentacosanoic (isocerotic)	86.6[fff], 86.9[a]
			Phthioic[ss] (3,13,23-trimethyltricosanoic)	20.5, $[\alpha]_D$ 22°
			Cerotic of beeswax	77.5–78[tta]
Heptacosanoic	$C_{27}H_{54}O_2$	87.6	DL-2-Methylhexacosanoic	73–73.7[ss], 75.5–76[xxx]
			D(+)-2-Methylhexacosanoic	69.8[vv]
			10-Methylhexacosanoic	54–55[aaa]
			24-Methylhexacosanoic (anteisoheptacosanoic)	72.9
			25-Methylhexacosanoic (isoheptacosanoic)	82[z]
			Carbocerotic[q]	82.5[q, p, eee]
Octacosanoic (*n*-Montanic)	$C_{28}H_{56}O_2$	90.5[kkk], 90.1–90.4[aaa]	D(+)-3-Methylheptacosanoic	73.1[ss]
			26-Methylheptacosanoic (isomontanic)	89.3[s], 86.7
Nonacosanoic	$C_{29}H_{58}$	90.3	27-Methyloctacosanoic (isononacosanoic)	84.4
			28-Methyloctacosanoic	76.1[eee]
			Montanic (natural)	86.0[r], 86.8[eee]
Triacontanoic (Myricinic) (*n*-Melissic)	$C_{30}H_{60}O_2$	93.7[vv], 93.1[kkk]	28-Methylnonacosanoic (isotriacontanoic)	90.1, 91

TABLE 9. (*Continued*)

N-Acid	Formula	M.P. (°C)	Isomer	M.P. (°C)
Hentriacontanoic	$C_{31}H_{62}O_2$	93.1	28-Methyltriacontanoic (anteisohentriacontanoic)	80.7
			29-Methyltriacontanoic (isohentriacontanoic)	90
			Melissic (natural)	90[ccc], 90.1[p]
Lacceroic	$C_{32}H_{64}O_2$	95.8	Isolacceroic	92, 89[u, ppp]
Ceromelissic	$C_{33}H_{66}O_2$	94.7	Psyllic	94[t, y]
Geddic	$C_{34}H_{68}O_2$	96.2, 98.2[vv]	Isogeddic	94.8
Ceroplastic	$C_{35}H_{70}O_2$	96–98[v]	33-Methyltetratriacontanoic (isoceroplastic)	95.6[fff], 92[w]

Note: Iso- acids have a branching group on the C atom next to the end of the chain.

[a]from wool degras by Weitkamp (1945); [b]prepared by Krafft (1879); [c]synthesized by Fordyce and Johnson (1933)[87]; [d]m.p. by Eisenstein (1920); [e]from egg yolk oil by Suzuki (1927); [f] from denatura oil by Meyer and Beer (1912); [g]m.p. by Holde and Gentner (1925)[59]; structure by Spielman (1934); [i]m.p. by Meyer; [l]m.p. by Shriner; [k]m.p. by Brigl; [l]first observed by Stürcke (1884); [m]m.p. by Betrabet; [n]derived from mycolic acid by Anderson and Chargaff (1929); [o]from beeswax by Gascard and Damoy; [p]m.p. by Damoy; [q]refers to the C_{27} acid of Brodie who first discovered it in Chinese insect wax (1848); [r]m.p. by Lüdecke; [s]from sticklac by Gascard who first named it, m.p. is that of the natural acid (1914); [t]first observed by Sundwik (1907)[140a]; [u]m.p. by Holde; [v]first observed by Koyama and termed ceroplastic (1935); [w]isolated by Power and Tutin from olive bark wax (1908); [x]ibotacerotic of Koyama (1935); [y]from *C. rubens* insect wax by Koyama (1935); [z]identity uncertain.

[aa]isolated by Anderson and Chargaff (1929); [bb]from cerebrosides by Levene and West (1913); [cc]from clematis by Power and Tutin (1914); [dd]as given in table by Markley[86]; [ee]from bayberry wax by McKay; [ff]m.p. by Taylor and Levene (*cf. Chem. Abstracts* **23**, 817 (1929); [gg]synthesized by Cason (1942)[17]; [hh]by Cason *et al.* (1944); [ii]mean values of Prout *et al.* (1948)[118]; [jj]by Prout and Cason (1949)[114]; [kk]by Cason and Prout (1944)[17a]; [mm]by Lipp and Kovács[80]; [nn]by Fischer and Schneider; [oo]by Levene and Taylor[82]; [pp]by Holde *et al.* (1929); [qq]by Ragon and Bolle (1948); [rr]by Meyer, Brod, and Soyka (1913)[100]; [ss]by Ställberg-Stenhagen (1949); [tt]derived from natural material; [uu]computed melting point; [vv]Ställberg-Stenhagen (1946); [ww]by Yamasaki[153]; [xx]by Robinson and Robinson; [yy]by Fischer and Schneider; [zz]by Weitzel, *A. F. et al.* (1949).

[aaa]setting pt. by Garner and Robinson: [bbb]mean value of m.pt. by Cason *et al.* (1950)[18]; [ccc]by Holde and Bleyberg (1930)[68, 68a]; [ddd]by Ställberg-Stenhagen (1951); [eee]by Tiedt and Truter; [fff]mean values m.pts. of Arosenius *et al.* (1948), cf. **C. A. 45**, 9472 (1951); [ggg]Schneider and Spielman[139a]; [hhh]listed by Deuel, Jr.[31]; [iii]by Weitkamp (1945); [jjj]by Cavanna (1950)[18a]; [kkk]by Murray and Schoenfeld (1953); [mmm]by Stenhagen and Tägstrom (1942); [nnn]mean values of m.p. by Cavanna and Ställberg-Stenhagen (1950)[18b]; [ooo]by Greer and Adams (1930); [ppp]by Kromer (1898) [qqq]by Morgan and Holmes (1927)[102]; [rrr]by Stenhagen and Tägstrom-Eketorp[135a]; [sss]by Ställberg-Stenhagen (1945); [ttt]mean of m.p. range of Cason, Adams, *et al.*[17b]; [uuu]m.p. by Levene and Taylor[84]; [vvv]by Asano and Ohta (1944), cf. **C. A. 45**, 4302; [www]by Asano *et al.* (1950), cf. *Chem. Abstacts* **44**, 1950; [xxx]mean m.p. of Schneider and Spielman (1942)[139a]; [yyy]by Pool and Ralston (1942)[118]; [zzz]by Bergmann and Swift (1951)[6a].

TABLE. 10 NEUTRALIZATION VALUES, DENSITIES, AND MOLAR VOLUMES OF NORMAL FAT AND WAX ACIDS

Carbon No.	Name of n-Acid	M.W.	Neutralization Value	Density at 100°C	Molar Volume[c] 100°C
10	Capric	172.26	325.69	0.8372[a]	205.75
12	Lauric	200.31	280.08	.8332[a]	240.41
14	Myristic	228.36	245.68	.8306[a]	274.93
16	Palmitic	256.42	218.80	.8286	309.46
18	Stearic	284.47	197.23	.8270	343.73
20	Arachidic	312.52	179.52	.8240[b]	379.27
22	Behenic	340.57	164.73	.8221[b]	414.27
24	Lignoceric	368.62	152.20	.8207[b]	449.15
26	Cerotic	396.68	141.44	.8198[b]	483.87
28	Montanic	424.73	132.09	.8191[b]	518.53
30	Melissic	452.78	123.91	.8185	553.18
32	Lacceroic	480.83	116.68	.8180	587.81
34	Geddic	508.88	100.25	.8176	612.62

[a]Experimental values by Dorinson *et al.*[39] at 80°C extrapolated. [b]Values by Bleyberg and Ulrich[10]. [c]Values computed from $V_m = M/d$, where V_m is the molar volume, M the molecular weight, and d the density, m/v.

TABLE 11. REFRACTIVE INDICES FOR THE HIGHER MONOETHANOID ACIDS

Acid	Refractive Index		Acid	Refractive Index	
Capric	(n_D^{40})	1.4288[c]	Arachidic	(n_D^{100})	1.4250[b]
Lauric	(n_D^{44})	1.4323[d]	Behenic	(n_D^{100})	1.4270[b]
Lauric	(n_D^{82})	1.4183[a]	Lignoceric	(n_D^{100})	1.4287[b]
Myristic	(n_D^{60})	1.4308[a]	Cerotic	(n_D^{100})	1.4301[b]
Palmitic	(n_D^{70})	1.4309[c]	Montanic	(n_D^{100})	1.4313[b]
Stearic	(n_D^{80})	1.4299[a]	Melissic	(n_D^{100})	1.4323[b]

[a]Values by Monick *et al.* (1942)[102]; [b]values by Bleyberg and Ulrich (1931)[10]; [c]value by Bagard (1907); [d]value by Iyer *et al.* (1925); [e]value by Dorinson *et al.* (1942).

The average expansion of stearic acid in the solid C form is 0.000262, solid B form 0.000269, and liquid C form 0.000973 ml/g/C.

Unsaturated Fatty Acids

The role which unsaturated fatty acids play in the chemistry of waxes is of *minor* yet significant importance. They are found in substantial percentages in liquid waxes of marine animal and of vegetable origin, and in very small percentages in some of the solid vegetable and insect waxes. The fatty acids with a double bond, that is the ethylenic acids, are called *monoethenoid acids*. They are found in nature only with an even number of carbons. Table 13 includes monoethenoid acids which are not natural. Those fatty acids which have two or more double bonds are termed *polyethenoid acids*. The most widely occurring polyethenoid acids in nature are *linoleic acid*, $CH_3(CH_2)_4CH{:}CHCH_2CH{:}CH(CH_2)_7COOH$, having two double bonds; and *linolenic acid*, (9,12,15-octadecatrienoic acid),

$CH_3CH_2CH{:}CHCH_2CH{:}CHCH_2CH{:}CH(CH_2)_7COOH$, having three double bonds. Linoleic and linolenic acids accompany oleic acid in fruit and flower waxes. *Eleostearic acid*, an isomer of linolenic acid, has its double bonds in conjugated positions, 9, 10; 11, 12; 13, 14. It is the principal acid of tung oil, but is also found in very small amounts in quite a few vegetable oils and tallows. Other polyethenoid acids with more than 3 double bonds, such as *clupanodonic acid*, $\Delta^{4,8,12,15,19}$-*docosapentaenoic acid*, are associated with marine animal oils not of the liquid wax type.

Ethinoic acids have a triple bond, exemplified by *taricic acid* (6,7-stearolic acid), $CH_3(CH_2)_{10}C{\equiv}C(CH_2)_4COOH$, which occurs in nature as

TABLE 12. MELTING POINTS (°C) OF SOLID KETO CARBOXYLIC ACIDS ($C_nH_{2n-2}O_3$)

Carbon No.	Position of CO Group						
	2	3[hh]	4	5	6	7	8
8	32–33[bb]	68.7	53[d]	34[b]	52[b]	29–30[b]	
9	43–44[r]	68.3	64–66[s], 69[c]	—	—	42[d]	—
10	46–47[bb]	79.7	68–69[s]	57–58	—	—	64[d]
11	55[bb], 59[dd]	78.8[s]	79.5–80[ff]		53–54[aa]	—	—
12	56.5–57[bb]	86.7	78.5–79[ff]		69?	—	68?
13	62–62.5[bb]	85.8	85.5–86[ff]	—	—	—	—
14	63.8[r]	91.2	87[n, o]		72.5[ee]	—	—
15	68–68.5[bb]	90.3	92.6[b]	—	—	—	—
16	69	95.2	91–92[k, l, m]	88[n]	—	78[n]	77–78[n]
17	—	95.3	—	—	—	—	74[y]
18	—	98.5	95[b]	—	87[e,q,k], 86[aa]	75[p]	—
20	78?	100.7	—	94?	89[aa]	—	85.6?
22	—	102.7	103[ee]	99	92–93[aa]	—	—
24	—	104.7	—	—	95–96[aa]	—	—
26	—	—	—	—	—	98?	97.5–98.5[aa]
	9	10	11	12	13	14	15
11	53–55[e]	58–59[e]					
12	50[ii]	72[z]	—				
13	—	63[n]		70–71[j]			
14	66[f]	—	—	—	75[w]		
15	—	—	70–71[i]	—	—	78.4–79.4[j]	
16	73.5–74.5[j]	75–75.8[m]	74–75[b]	91–92[b]	—	—	—
17	78.5[k]	—	—	—	—	—	—
18	83[r]	82.4[x, m], 83[k]	—	81[s]	—	—	—
19	—	86–87[e]	—	—	—	—	—

TABLE 12 (*continued*)

Carbon No.	Position of CO Group						
	10	11	12	13	14	15	16
20	89?	—	—	86?	—	—	—
21	—	—	—	89–90[t]	—	—	—
22	94[o]	—	—	—	—	—	—
23	93.5	—	—	—	—	—	—
24	94–94.5[ff]	—	—	95[o]	—	—	—
26	66	66	66	99?	—	—	—
28	—	—	—	101.5?	—	—	—
29	101–101.5[h]	—	—	—	—	—	—
30	—	102[h]	89[h]	104[w]	—	—	—
31	—	—	105–105.3	—	—	—	—
32	105–106	—	—	105–105.6[h]	—	—	—
33	—	—	—	—	105–105.5[h]	—	—
34	—	—	—	107.7[aa]	—	106–106.8[h]	—
35	—	—	—	107.7[y]	—	—	—
42	—	—	—	110[r, w]	—	—	106–106.5[h]

9-ketoöctacosanoic acid has a melting point of 100°C[h].

9-ketoeicosanoic acid has a melting point of 78–80°3[cc].

[a]f.p. of 3-ketocaprylic acid, $CH_3(CH_2)_4 \cdot CO \cdot CH_2CO_2H$; [b]listed by Ralston[118]; [c]m.p. by Lukeš (1930); [d]by Blaise and Koehler; [e]by Abraham *et al.*; [f]by Ames *et al.*[2a]; [g]by Paraskova; [h]by Jones[67]; [i]by Davies and Adams; [j]by Chuit *et al.*[21]; [k]by Robinson, G. M., and Robinson, R[120]; [l]by Houston[62]; [m]by Fordyce and Johnson[37]; [n]by Robinson, G. M.[122]; [o]by Robinsons; [p]f.p. by Arnaud; [q]lactarinic acid from dried fungi[110]; [r]listed by Markley[96]; [s]m.p. by Perrotte; [t]by Le Sueur and Withers[82]; [u]by Schuette *et al.* (1948); [v]by Myddleton and Barrett (1927); [w]by Mrs. Robinson[121]; [x]various melting points averaged: 82.4°[37], 77°[120], 83°[96], 80.1°C (f.p.)[96]; [y]by Bodenstein; [z]by Breusch and Keskin[13]; [aa]by Fieser and Scmuszkovics (1948);[35] [bb]by Adickes and Andresen[2]; [cc]by Zhukov and Shestakov[154]; [dd]by Chuit and Hausser (1926)[20]; [ee]m.p. by Asano and Ohta (1945), cf. C. A. 45, 4302; [ff]m.p. by Schneider and Spielman (1942)[129a]. [gg]by Francis, King, and Willis[40]; [hh]by Stenhagen (1951); [ii]by Asano[4].

glyceride of certain seed fats; they are not found in waxes. Substituted unsaturated fatty acids are associated with glycerides in fats and oils and not with waxes.

Hexacosadienoic acid, discovered by Bergmann and Swift[8a] in sponges, is described as crystallizing in glistening waxy plates, which melt at 61.4–61.8°C. The structure assigned to this acid is $AmCH{=}CHCH_2CH{=}CH(CH_2)_{15}CO_2H$.

Ethylenic Fatty Acids. The unsaturated monocarboxylic acids with a double union of carbons are termed ethylenic fatty acids, or monoethenoid acids; those in the range of C_{12} to C_{30} with an even number of carbons are listed in Table 13. Of the dodecenoic acids (C_{12}) at least three occur in natural fats, namely 4-dodecenoic in small amounts in oils of a few tropical

plants; 5-decenoic in the head and blubber oils of whales; and 9-dodecenoic in cochineal fat, Japanese coccid wax, and in milk fat. 3-dodecenoic acid is a liquid.

Of the tetradecenoic acids at least three have been identified in the natural fats: 5-tetradecenoic (*physeteric acid*) is a liquid found in a number of marine oils; 9-tetradecenoic (*myristoleic acid*) is also found in animal fats, depot fats, and in some marine oils; 4-tetradecenoic (*tsuzic acid*) occurs in seed oils of tropical plants.

Of the hexadecenoic acids only two have been observed in fats or waxes of natural origin; one is 7-hexadecenoic (*hypogaeic acid*), a constituent of beeswax; the other is 9-hexadecenoic (*palmitoleic acid*), a major component of many of the marine oils. It is solid only in the isomeride form, namely *gaidic acid*. *Hypogaeic acid* has the formula structure $CH_3(CH_2)_7$-$CH{=}CH(CH_2)_nCOOH$, where $n = 7$. The same position of the double union of carbons from the terminal CH_3 group holds for the higher monounsaturated natural vegetable acids[11], such as oleic, eicosenoic (of jojoba wax), erucic, selacholeic, ximenic, etc.

Of the octadecenoic acids, *oleic acid* is the most noteworthy. It occurs in nature more abundantly than any other fatty acid. Very small percentages are found in vegetable waxes; but substantial proportions occur in the marine oils, a few of which are classed as liquid waxes. When oleic acid is carefully oxidized (Grün and Wittka process) it yields pelargonic acid, $CH_3(CH_2)_7COOH$, and *azelaic acid* (m. 106.5°C), $HOOC(CH_2)_7COOH$, and hence the positional formula of oleic acid is $CH_3(CH_2)_7CH{=}CH(CH_2)_7$-$COOH$[52]. Oleic acid reacts with alkaline permanganate to form *cis*-9,10-dihydroxystearic acid. Oleic acid crystallizes in needles (m. 13.4°C, α form) and may change by slow crystallization into the β form (m. 16.3°C) which is the more stable.

The 2-, 3-, 4-, 5-, 7-, and 8-octadecenoic acids have been synthetically prepared by investigators, but are not generally present in the naturally occurring fats or waxes; *2-octadecenoic acid* has been identified in the oleic acid constituent of palm oil. The 13- and 14-octadecenoic acids have not been discovered in nature, nor have they been synthesized. *Petroselinic acid* (*cis*-6-octadecenoic acid) was first isolated from parsley seed oil and later found to be the principal constituent of seed fats of the *Umbelliferæ* and and *Araliaceæ* families. *Vaccenic acid* (11-octadecenoic) is unique in its growth-promoting properties and is associated with animal fats; *12-octadecenoic acid* has been found in partially hydrogenated peanut oil.

At least two eicosenoic acids occur in natural fats and oils; one is 11-eicosenoic acid, which is in the *cis*-form (m. 22°C, n_D^{25} 1.4600) combined with its corresponding monoethenoid alcohol and comprises one of the constituents of the liquid wax (jojoba oil) obtainable from the evergreen

shrub, *Simmondsia californica* L. It is associated with the *docosenoic acid* ester. The other is 9-eicosenoic (*gadoleic acid*), widely distributed in the marine animal and fish oils.

Two docosenoic (C_{22}) acids have been isolated from natural fats; 13-docosenoic (*erucic acid*) in certain seed fats, and 11-docosenoic (*cetoleic acid*) in the marine oils, including the liquid waxes. The treatment of erucic acid with nitrous acid, or dilute nitric acid, converts it to the *trans* isomer, *brassidic acid*. Cetoleic is generally accompanied by gadoleic acid in marine oils. 15-Tetracosenoic is known as *selacholeic acid* as it occurs in marine liver oils, and *nervonic acid* as it occurs in the cerebrosides of brain material. 17-Hexacosenoic (*ximenic acid*) is found in the tallownut, *Ximenia americana*, L., together with *21-triacontenoic acid*, (lumequeic acid) $CH_3(CH_2)_7CH{:}CH(CH_2)_{19}COOH$. The C_{28} acid, 19-octacosenoic acid, homolog of the C_{26} and C_{28} acid, is also probably a vegetable acid. Both C_{24} and C_{26} monoethenoid acids (m. 39°C, and m. 45–45.5°C) have been isolated from the lipides extracted from the mycelium of *Phycomyces blakesleeanus* by Bernhard and Albrecht[9].

Linoleic acid, a C_{18} acid with two double unions, and *linolenic* with three double bonds often accompany oleic acid in fruit and flower waxes. In linoleic acid (m. −5.1°C) the double bonds are located at the $\Delta^{9,10}$ and $\Delta^{12,13}$ positions as shown in the structure $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$. In linolenic acid (m. −11.2°C) the double bonds are located at the $\Delta^{9,10}$, $\Delta^{12,13}$, and $\Delta^{15,16}$ positions: $CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$.

Ricinoleic acid is a hydroxy monoethenoid acid encountered in vegetable oils, particularly castor oil, but not in waxes. It has the structure $CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOH$. Ricinoleic acid is optically active, $[\alpha]_D = 6.7°$.

Stereoisomerism of Acids

In the monoethenoid series, isomers are plentiful because shifting of the double bond takes place, often by the mere application of gentle heat, and also because of stereoisomerism (*cis-trans*) at the position of the double bond. Stereoisomerism, or space isomerism, may be optical when the molecules of two compounds, in three space dimensions, have special structures which are mirror images and are not superposable. Such isomers rotate a plane of polarized light passed through them. From a geometrical point of view the structures of optical isomers are asymmetric. In structures which contain asymmetrically carbon atoms attached to each other by a double bond, we have stereoisomerism, known as geometric or *cis-trans* isomerism, common to the series of monoethenoid acids found in nature.

TABLE 13. MONOETHENOID ACIDS, $C_nH_{2n-2}O_2$

	Double Bond in the $\Delta^{9,10}$ position for terminal CH_3 end	Positional and Geometric Isomerides
$C_{12}H_{22}O_2$	3-dodecenoic (liquid) (lauroleic)	2-dodecenoic, b_2 164–165°C[118], m. 15°C 4-dodecenoic (linderic) m. 1–1.3°C[71] 5-dodecenoic, m. 12°C, b_{15} 165°C, d^{18} 0.9130 6-dodecenoic, m. 61–62°C (α), 40–41°C (β form) 11-dodecenoic m. 19°C[21], b_{12} 171–172°C[21]
$C_{14}H_{26}O_2$	5-tetradecenoic (liquid) (physeteric) $b_{190-200}$°C, d_4^{15} 0.9081	2-tetradecenoic m. 33°C 4-tetradecenoic (tsuzuic) m. 18–18.5°C[71] 5-tetradecenoic b_{15} 190–195°C[146] *cis*-9-tetradecenoic (liquid) (myristoleic)[14a] m. −4.5 to 4°C *trans*-9-tetradecenoic m. 18–18.5[14a]
$C_{16}H_{30}O_2$	7-hexadecenoic, m. 21°C[118a]	2-hexadecenoic m. 45°C (gaidic) *cis*-9-hexadecenoic (palmitoleic) m. 0–1°C (α-), m. 16.3°C (β-form) *trans*-9-hexadecenoic m. 32.3°C (α-), 41°C (β-form) (physetoleic, zoömaric)
$C_{18}H_{34}O_2$	*cis*-9-octadecenoic (oleic) m. 9.8–10.4°C[50] 10.9–11.5°C[62a], m. 13.4° (α); m. 16.3°C (β-form[98]), b_{100} 286°C *trans*-9-octadecenoic (elaidic) m. 39.7–40.1°C[50], 44.5–45.5°C[62a]	*cis*-2-octadecenoic m. 50.5–51°C *trans*-2-octadecenoic, m. 58–58.5°C, $\Delta^{\alpha,\beta}$-oleic *cis*-3-octadecenoic, m. 56–57°C, $\Delta^{\beta,7}$-oleic *cis*-4-octadecenoic, m. 52–53°C, 41[14a] *trans*-4-octadecenoic, m. 58–59°C[14a] *cis*-5-octadecenoic, m. 42–43°C[118] *trans*-5-octadecenoic, m. 47.5°C[118] *cis*-6-octadecenoic, m. 33°C (petroselenic) *trans*-6-octadecenoic, m. 53°C (petroselaidic)[98] *cis*-7-octadecenoic, m. 11.8–12.5°C[62a] *trans*-7-octadecenoic, m. 43.5–44.5°C[62a] *cis*-8-octadecenoic, m. 22.7–23.8°C[62a] *trans*-8-octadecenoic, m. 51.5–52.3°C[62a] *cis*-10-octadecenoic, m. 22.2–22.8°C[62a] *trans*-10-octadecenoic, m. 52–52.6°C[62a] *cis*-11-octadecenoic, m. 13–14°C[62a] *trans*-11-octadecenoic, m. 43.5–44.5°C[62a] *cis*-12-octadecenoic, m. 26.8–27.6°C[62a] *trans*-12-octadecenoic, m. 52–53°C[62a] *trans*-15-octadecenoic, m. 61–61.5°C *trans*-16-octadecenoic, m. 62.8–63.5°C *trans*-17-octadecenoic, m. 55.3°C

TABLE 13. (*continued*)

	Double Bond in the Δ^{n-1} position from terminal CH_3 end	Positional and Geometric Isomerides
$C_{20}H_{38}O_2$	*cis*-11-eicosenoic (of jojoba wax), m. 22°C[61]	9-eicosenoic
	trans-11-eicosenoic, m. 52–53°C[61]	*cis*-gadoleic, m. 24.5°, 23–23.5°C[14a]
		trans-gadoleic, m. 53–54°, 54°C[14a]
		isogadoleic, m. 65.8°C
		gondoic (marine oils), m. 32.5–34°C
$C_{22}H_{42}O_2$	*cis*-13-docosenoic (erucic), m. 32.8°[144], 33.5°C[118]	9-docosenoic (of rapeseed oil), m. 54.8°C
	trans-13-docosenoic (brassidic), m. 60.8°C (α), m. 65–66°C (β-form)	11-docosenoic[144], 32.5–33°C (cetoleic, of marine animal oils)
$C_{24}H_{46}O_2$	*cis*-15-tetracosenoic (selacholeic), m. 42–5–43.2°C, nervonic, m. 40–41°C[70]	2-tetracosenoic, m. 59°C[100]
		cis-5-tetracosenoic, m. 41.1°C
	trans-15-tetracosenoic, m. 66–67°, 61°C[118]	*trans*-5-tetracosenoic, m. 70.5°C
		17-tetracosenoic, m. 39°C[8]
$C_{26}H_{50}O_2$	17-hexacosenoic (ximenic),[11] m. 45–45.5°C[9]	9-hexacosenoic (of sponges)[8a], m. 86.8–87.5°C
$C_{28}H_{54}O_2$	19-octacosenoic, m. 53°?C	?-octacosenoic (of sponges)[8a], m. 57.3–57.8°C
$C_{30}H_{58}O_2$	21-triacontenoic (lumequeic)[11], m. 60°?C	?-triacontenoic, m. 84°C

Note: Vaccenic acid (*trans*-11-octadecenoic acid) has a melting point variously reported as 38.5–39°[96], 42.5, 43–44, 41–42, and 43.5–44.5°C.

The relation of oleic acid to its stereoisomer *elaidic acid* is shown below:

$$\begin{matrix} HC\cdot(CH_2)_7\cdot CH_3 \\ \| \\ HC\cdot(CH_2)_7\cdot COOH \end{matrix} \qquad \begin{matrix} CH_3\cdot(CH_2)_7\cdot CH \\ \| \\ HC\cdot(CH_2)_7\cdot COOH \end{matrix}$$

cis-oleic acid — *trans-oleic acid or elaidic acid*

The *cis*- acids of the monoethenoid series in Table 13 have melting points which range between >0 and 34°C for the C_{16}- to C_{22} acids, whereas the melting points of the corresponding *trans*-acids range between 28 and 65°C, or about 30°C higher for the geometric rearrangement from *cis*- to *trans* spacings.

Optical Isomerism. Optical isomerism, detected by measuring the degree to which a given substance is capable of rotating a plane of polarized light, occurs in saturated acids with an alkyl side chain, such as the *lano*-acids found in wool fat. The isomer which rotates a plane of polarized light to the right is called dextrorotatory and the one which rotates it to the left levorotatory.

When an H atom of the polymethylene chain of a fatty acid is replaced

by another atom or radical there is produced in the molecule an asymmetric carbon atom and a plane of asymmetry. A number of saturated hydroxy acids are known to occur naturally, and are optically inactive because they contain equal amounts of the *dextro-* and *levo*-isomers; the optical effect of one form is neutralized by that of the other. Such a product is known as a *racemic* modification and is designated as a DL-form. *Lanopalmic acid*, the α-hydroxyisopalmitic acid constituent of wool wax, is strongly dextrorotatory $[\alpha]_D^{20} + 5.23$. *Tuberculostearic acid*, a constituent of the lipide wax of tubercle bacilli, has a methyl side chain in the 10 C position, has very little or no rotation, and is considered a DL-form.

A compound which may be optically inactive because of internal compensation, but which would otherwise be optically active is said to have a *meso*-form, and will differ in its physical properties from the DL-form. The optical activity of alkyl-, hydroxy-, and halogen-substituted aliphatic acids will range from extremes of *levo-* to *dextro-* degrees of rotatory power according to the position of the assymetric carbon atom to which the side chain group is attached, and is influenced by the length of the polymethylene straight chain.

Dicarboxylic Acids

Dibasic aliphatic acids (also termed polymethylene dicarboxylic acids and dioic acids) are only occasionally encountered as such in waxes, but do play an important part in plant metamorphosis, as do the corresponding dihydric alcohols. Those dioic acids having COOH groups located at opposite ends of the methylene chain (α, ω), HOOC—C_nH_{2n}—COOH, and an odd number of carbons, are perhaps the most important ones to consider, although dioic acids with an even number of C atoms are occasionally found, e.g., C_{18} and C_{22} dioic acids and their hydroxy derivatives, in the waxy substance of the bark of *Quercus suber*, and C_{22} in japanwax. The water solubilities (g per 100 g water) of the dicarboxylic acids is of the following order: C_5 63.9 (at 20°C), C_6 1.5 (at 15°C); C_7 2.5 (at 20°C); C_8 0.16 (at 20°C); C_9 0.2 (at 15°C); C_{10} 0.1 (at 15°C). As a whole, dioic acids with an odd number of carbons are always more soluble than those with an even number. The aqueous solutions of dioic acids are of strongly acid character. The acids crystallize in monoclinic form.

The high molecular weight dioic acids become increasingly unstable to heat. When heated, the acid either yields an anhydride (low in m. p.), or carbon dioxide is eliminated and a monobasic acid formed. Most of the dicarboxylic acids can be volatilized *in vacuo*. The behavior of *n*-dicarboxylic acids with an odd number of carbons differs from that of the even-numbered acids. In scanning the series of acids enumerated in Table 14 it will be at once apparent that the melting points gradually increase with

each succeeding odd-acid, whereas with even-acids the first acid (not shown), *succinic acid* HOOC—$(CH_2)_2$—COOH (m. 185°C), starts with a high-melting point, followed by *adipic acid* HOOC—$(CH_2)_4$—COOH (m. 153°C), and the melting points descend gradually as the series ascends.

TABLE 14. POLYMETHYLENE DICARBOXYLIC ACIDS

Carbon No.	$C_nH_{2n-2}O_4$ (α, ω)	Chain Length (Å)	M P. (°C)	B.P. (°C)		
				100	15	10 mm
5	Glutaric		97.5, 98.05[b]	258?	—	—
6	Adipic	10.02[f]	153.05[b]	265[a]	216.5[a]	205
7	Pimelic	22.12[f]	103, 105.75	272[a]	223[a]	—
8	Suberic COOH·$(CH_2)_6$·COOH	12.58[f]	140.5[b], 140[i]	279[a]	230[a]	—
9	Azelaic	27.14	106.5[q], 107.0[c]	286.5[a]	237[a]	226
10	Sebacic	15.02[f]	133.0[i]	294.5[a]	243.6[a]	—
11	Undecanedioic	—	111[d]	—	—	—
12	Dodecanedioic	—	128[d], 129[i]	—	245_{10}[p]	—
13	Brassylic	37.95[f]	113.1[d], 114.6	—	—	—
14	Tetradecanedioic	—	125.8[d], 126.5[i]	—	—	—
15	Pentadecanedioic	—	114.7[d], 114.5[q]	—	—	—
16	Hexadecanedioic (thapsic)	—	124.1[d], 125[i]	—	—	
17	Roccelic	—	118.0[d]	—	—	
						0.3 mm.
18	Octadecanedioic	25.10[f]	124.7[d], 124[i]	—	—	106
19	Nonadecanedioic	—	119.2[d]	—	—	113
20	Eicosanedioic	—	122.5–124.5[m]	—	—	
21	Heneicosanedioic (japanic)	—	123.5	—	—	117–117.5[g]
22	Docosanedioic	—	123.8[i], 126[k], 127[o]	—	—	—
23	Tricosanedioic	—	127.5[i]	—	—	—
24	Tetracosanedioic	32.8[h]	123.0, 127[o]	—	—	—
26	Hexacosanedioic	35.0[h]	123.0	—	—	—
28	Octacosanedioic	37.1[h]	123–125	—	278	—
30	Triacontanedioic	39.4[h]	123.5[i]			
32	Dotriacontanedioic	—	123[i]			
34	Tetracontanedioic	44.85[h]	123[i]			
36	Hexacontanedioic	45.65[h]	—			

[a] B.p. by Krafft and Noerdlinger[76a]; [b]m.p. by Serwy[131]; [c]m.p. by Normand *et al.*[110]; [d]mean of m.p. by Chuit[19a]; [e]m.p. by Tsujimoto[146]; [f]crystal spacing by Hendricks[65]; [g]b.p. by Schaal[129]; [h]crystal spacing by Francis *et al.*; [i]m.p. by Fairweather[31]; [j]m.p. by Flaschentrager and Halle[36]; [k]m.p. 125.7–126.3°C by Siina (1940)[131a]; [m]m.p. by Drake *et al.*[30], natural source 122.5–124.5°C, synthetic 121–123°C; [n]m.p. by Kerschbaum (1927)[68] [o]m.p. by Siina (1939); [p]b.p. by Noerdlinger (1890); [q]mean m.p. of Bergmann & Swift (1951)[8a], natural source; [r]m.p. by Grün and Wittka[62].

This causes the even-members of the series to converge with the odd-members at about 124°C, when the C_{23} acid is reached. An explanation of this phenomenon lies to some extent in the nature of the crystal cell of the dicarboxylic acids. Those with an even number of C atoms in the chain have but two molecules packed in the unit cell, whereas those with an odd number have four.

The unit cell spacings of the dicarboxylic acids are given in Table 14 were determined by Caspari by the x-ray rotating or oscillating crystal method. The unit cells have nearly constant *a* and *b* axes; as regards the *c* axis the acids fall into two groups, one having the moles of an even number of C atoms, and the other those of an odd number. The *c* axis of the even-numbered mols is proportional in length to the number of C atoms; for the odd-numbered mols it is proportional to twice the number of C atoms. In the latter group, two molecules lie end to end in the cell along the *c* axis. Examples of unit cell construction are given below.

Acid	Å length (10^{-8} cm)				Moles per Unit Cell
	a	*b*	*c*	*β* angle	
C_{10} Sebacic	10.08	4.96	15.02	133° 50′	2
C_{13} Brassylic	9.63	4.82	37.95	128° 20′	4
C_{18} Octadecanedioic	9.76	4.92	25.10	131° 10′	2

Mean difference of 1.52 Å between carbons.

The dicarboxylic acids listed in Table 14 are normal, that is those with the α, ω polymethylene carboxyl groups, but there do exist many isomers. The peculiar behavior of the dicarboxylic acids is not shown in their dialkyl ester derivatives since the dimethyl and diethyl esters of both even and odd C content increase in melting point in a regular manner with ascending chain length.

The dicarboxylic acids play an important metabolism role in the formation of *etholide waxes* in plants, such as the wax in pine needles, involving reactions of the dicarboxylic acid with ω-hydroxy fatty acid. An etholide wax (m. 75°C) has been prepared synthetically by reducing the dimethyl ester of tetradecanedioic acid, resulting in a condensation product of ω-hydroxylauric acid and the free dicarboxylic acid.[19]

Sometimes dicarboxylic acids are formed by the disruptive oxidation of monoethenoid fatty acids whence the *di-* is accompanied with a *mono-*carboxylic acid of lower molecular weight, commonly *nonanoic acid* (pelargonic acid). For example, *erucic* (C_{22}) forms nonanoic (C_9) and *brassylic*, $HOOC(CH_2)_{11}COOH$; *selacholeic* (C_{24}) forms nonanoic and *heptadecanedioic* (C_{17}); and *tricontenoic* (C_{30}) forms nonanoic and heneicosanedioic (C_{21}), known also as japanic acid, the principal constituent of japanwax. *Pentadecanedioic*, also called tridecamethylene-1,12-dicarboxylic acid, has

two well known isomers: diisobutylpimelic and diisoamylglutaric acids. The C_{18} dicarboxylic acid, *thapsic*, has an isomer, as do *roccelic* and *octadecanedioic*. *Nonadecanedioic* has two isomers, cetylmalonic and dioctylmalonic acids. *Japanic acid* (C_{21}) has an isomer known as octadecylmalonic acid. The C_{22} acid apparently occurs in nature only in the isomeric state, as *nonadecylmalonic acid*. The C_{24} acid is known best as the isomer, *eicosylsuccinic acid*. The C_{25} acid, *carnaubandioic* (m. 102.5°C), is reported as having been obtained by the oxidation of the dihydric alcohol, $C_{25}H_{52}O_2$, from carnauba wax, but its structure, that of docosylmalonic acid, $HOOC \cdot CH(CH_2)_{21}CH_3COOH$, has not as yet been fully established. The C_{27} acid in the series is an isomer known as tetracosylmalonic acid. The C_{34} acid, *tetratriacontanoic* (1, 32) has been prepared by Fairweather.[33] Still higher acids are known, e.g., a C_{35} acid (dicetylmalonic) and a C_{38} acid (dicetyladipic), both of which are isomers of the normal acids.

Unsaturated dioic, hydroxy dioic, dihydroxy dioic, and polyhydroxy dioic acids are more closely allied with sugars and starches, and are rarely encountered in waxes. *Shellolic acid* and similar acids found in shellac, and present in shellac wax as an impurity, are hydroxy derivatives of the unsaturated dicarboxylic acids of very high molecular weight.

Dicarboxylic acids with alkyl side chain linkings have been prepared by Ruzicka and also by Chuit and co-workers of the C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, and C_{17} members of the series. A dicarboxylic acid with an alkyl side chain melts at an appreciably lower temperature than the corresponding acid with an unbranched chain. For example, Chuit *et al.*[21] have reported the melting points of the C_{16} methyl polymethylenedicarboxylic acids as follows:

	M.P. (°C)
1-methyltridecane-1,13-dicarboxylic acid	93–94
2-methyltridecane-1,13-dicarboxylic acid	76–77
3-methyltridecane-1,13-dicarboxylic acid	62–63
4-methyltridecane-1,13-dicarboxylic acid	54–55

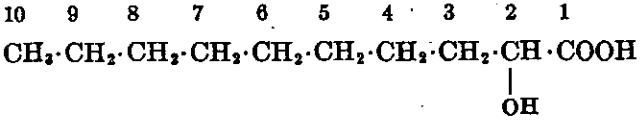
The location of the CH_3 group makes less difference in melting points of the odd C acids; e.g., β-methylthapsic (C_{17}) melts at 77.2–77.4°C, γ-methylthapsic at 78–78.4°C, and δ-methylthapsic at 78.8–79°C.

Note: The terms dicarboxylic and dioic are not synonymous, e.g., the C_{22} dibasic acid is either termed *eicosane dicarboxylic acid*, or preferably *docosanedioic acid*; the first name denotes a 20°C methyl chain attached to two CO_2H groups, whereas the second name indicates the total number of carbons in the dibasic acid.

Hydroxy Acids

Hydroxy acids are not uncommon constituents of the natural waxes. Dihydroxy and trihydroxy acids occasionally occur as wax constituents. All of the hydroxy acids encountered in waxes have more than 8 carbon

atoms, and with but few exceptions are of the saturated type, e.g.,



α-hydroxycapric acid (2-hydroxydecanoic acid)

When the hydroxyl (OH) group is attached to the C atom adjoining the terminal carboxylic (COOH) group, the acid is called an *alpha*-hydroxy acid, or specifically α-hydroxy-*n*-carboxylic acid. When the OH group is attached to the number 3 carbon atom, the acid is called a *beta*-hydroxy acid, to the number 4 carbon atom a *gamma*-hydroxy acid, and so on. The hydroxy acid with an OH group in a position farthest from the COOH group is termed an *omega*-hydroxy acid (ω-hydroxy-*n*-carboxylic acid).

	α	β	γ	δ	ε	ζ	η	θ	ι	κ	λ	μ	ν	ξ	ο	ω
Carbon position	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16 . . . last	

The α, β, γ designations are commonly employed, but the numeral designations as given in Table 15 have come into broad usage for all substituted groups in the fatty alcohols and acids. When the OH of a hydroxy acid is in the ω position it is obvious that the compound acts as an alcohol as well as an acid, since the OH derivative is in the form of the primary alcohol group (CH_2OH). The ω acids play an important role in the metabolism changes in the conifers, and are found in the waxes of conifers, generally accompanied by corresponding lactones and polyetholides. Gamma- and delta-hydroxy acids are quite unstable and split off a molecule of water readily to form *lactones*.

The positions of the OH groups in the dihydroxy acids have in the past been designated by Greek letter prefixes, but they are now commonly designated by numbers. The hydroxy acids are, generally speaking, oxidation products of unsaturated acids. As in hydroxy acids the number 1 position is assigned to the carbon of the COOH group; hence 2,3-dihydroxy denotes that the attachment of the OH groups is at the two carbon atoms directly adjoining the COOH group. Dihydroxy acids show the phenomenon of *cis-trans* addition isomerism, corresponding in a measure to the isomeric forms of the unsaturated acids from which they may be derived. For example, the *cis* addition, or *threo* form (m. 95°C) of 9,10-dihydroxystearic acid corresponds to elaidic acid, while the *trans* addition, or *erythro* form (m. 132°C) corresponds to oleic acid.

As a rule the melting points increase with the number of oxygen atoms introduced in the molecule. The *cis* and *trans* addition products derived from unsaturated acids have lower and higher melting forms, sometimes

TABLE 15. HIGHER HYDROXY AND DIHYDROXY ACIDS OF MONOETHANOID SERIES

Total Carbons	Monohydroxy Acids $C_nH_{2n}(OH)\cdot COOH$	M.P. (°C)	Dihydroxy Acids $C_nH_{2n-2}(OH)_2COOH$	M.P. (°C)
(8)	2-hydroxycaprylic	69.5(f.p.)[118]		
	3-hydroxycaprylic	38–38.5[3]		
	6-hydroxycaprylic	viscous liquid[118]		
	8-hydroxycaprylic	58[19]		
(9)	2-hydroxynonanoic (2-hydroxypelargonic)	70(f.p.)[118]	2,3-dihydroxypelargonic	119[c]
	3-hydroxynonanoic	59.5[a], 58.5[c], 48–51(f.p.)[118]		
	4-hydroxynonanoic	53–54[92]		
	9-hydroxynonanoic	69–70[12], 70.5[5]		
(10)	2-hydroxycapric	56–56.5[3]	2,3-dihydroxycapric	121–123[12]
	3-hydroxycapric	not stable, forms lactone		
	4-hydroxycapric	75.5[d] (forms di- and trimeric lactones)		
	10-hydroxycapric	72, 69 (f.p.)[5]		
(11)	2-hydroxyundecanoic (2-hydroxyhendecanoic)	73–73.5[3]	2,3-dihydroxyundecanoic	124–125[12]
	3-hydroxyundecanoic	49–50[51], 34 (lactone)[154]		
	4-hydroxyundecanoic	68[c], 69[5]	*threo*-9,10-dihydroxyundecanoic	82–83[14a]
	11-hydroxyundecanoic	76, 73–74 (f.p.)[51]	2,3-dihydroxylauric	125–126[12]
(12)	2-hydroxylauric	70–70.5[3]	4,5-dihydroxylauric	102
	3-hydroxylauric	62.5–63.5[21], 63[123]		
	4-hydroxylauric	78–79[23a]		
	11-hydroxylauric	84[f]		
	12-hydroxylauric (sabinic)			
(13)	2-hydroxytridecanoic	79.3, 78(f.p., LeSueur)[51]		
	4-hydroxytridecanoic	66–66.5[21], 66[123]		
	11-hydroxytridecanoic	28–29		
	13-hydroxytridecanoic	79–79.5[19], 77–78[92]		
(14)	2-hydroxymyristic	82, 81.5–82[21]	2,3-dihydroxymyristic	125–126[12]
	3-hydroxymyristic	78, 72–73 (f.p.)[142]	3,11-dihydroxymyristic (ipurolic)	127.5
	4-hydroxymyristic	34[29], (lactone)		
	11-hydroxymyristic	51, 55[e]	5,6-dihydroxymyristic	118–119[146]
	14-hydroxymyristic	91–91.5[19]	*threo*-9,10-dihydroxymyristic	80[14a]
			erythro-9,10-dihydroxymyristic	123–124[14a]

TABLE 15 (*continued*)

Total Carbons	Monohydroxy Acids $C_nH_{2n}(OH)\cdot COOH$	M.P. (°C)	Dihydroxy Acids $C_nH_{2n-1}(OH)_2COOH$	M.P. (°C)
(15)	2-hydroxypentadecanoic	84.5[51]	4,12-dihydroxypentadecanoic	
	4-hydroxypentadecanoic	51		
	10-hydroxypentadecanoic	63.7		
	11-hydroxypentadecanoic	63.5–64[27]		
	14-hydroxypentadecanoic	81–82[123]		
	15-hydroxypentadecanoic	84.8–85.2[18]		
(16)	2-hydroxypalmitic	86.5–87 (f.p.)[51]	2,3-dihydroxypalmitic	126
	3-hydroxypalmitic	83–83.5[121]	3,12-dihydroxypalmitic	83.4
	4-hydroxypalmitic	79–79.6[62]	7,8-dihydroxypalmitic	115
	7-hydroxypalmitic	73.7–74.2	7,16-dihydroxypalmitic	83–84[63]
	10-hydroxypalmitic	63.7	*threo*-9,10-dihydroxypalmitic	86.5[a]
	11-hydroxypalmitic (*dl*-jalapinolic)	68–69	*erythro*-9,10-dihydroxypalmitic	124.3[b]
		67.5–68[v]	9,16-dihydroxypalmitic	99–101[63]
	12-hydroxypalmitic	73.8–74.2[118]		
	13-hydroxypalmitic	89[109, 63]		
	14-hydroxypalmitic	91–92?		
	15-hydroxypalmitic (juniperinic)	93–94[123]		
	16-hydroxypalmitic (juniperic)	93.4[1], 91[62] 86.5–87 (f.p.)[118]		
(17)	2-hydroxymargaric	89[51]	2,3-dihydroxymargaric	127–130
	4-hydroxymargaric	58?		
	9-hydroxymargaric	60–61[19]		
	17-hydroxymargaric	87.5–88[19]		
(18)	2-hydroxystearic	91–92[51]	2,3-dihydroxystearic	125.5–126[b]
	3-hydroxystearic	85[117], 89[112]	*threo*-6,7-dihydroxystearic	114
	4-hydroxystearic	79–79.5[62]	*erythro*-6,7-dihydroxystearic	122[48, 96]
	5-hydroxystearic	54.5	*threo*-7,8-dihydroxystearic	95–96[62a]
	7-hydroxystearic	82[v]	*erythro*-7,8-dihydroxystearic	132–133[62a]

TABLE 15 (*continued*)

Total Carbons	Monohydroxy Acids $C_nH_{2n}(OH)$-COOH	M.P. (°C)	Dihydroxy Acids $C_nH_{2n-1}(OH)_2COOH$	M.P. (°C)
	8-hydroxystearic	81[143]	*threo*-8,9-dihydroxystearic	96–97[62a]
	9-hydroxystearic	74–75[143]	*erythro*-8,9-dihydroxystearic	118–119[62a]
	10-hydroxystearic (rosilic)	78.8[j]	*threo*-9,10-dihydroxystearic	95[k], 93–94[62a]
			erythro-9,10-dihydroxystearic	132.1[l]
	11-hydroxystearic	76–77[143]	D-9,12-dihydroxystearic	90[49, 125]
	12-hydroxystearic	78–79[143], 80.5–81[140]	DL-9,12-dihydroxystearic	69.5[49]
	13-hydroxystearic	77–77.5[143]	*threo*-10,11-dihydroxystearic	98–99.5[62a]
	14-hydroxystearic	76.5	*erythro*-10,11-dihydroxystearic	120–121[62a]
	16-hydroxystearic	81	*threo*-11,12-dihydroxystearic	94.5–96[62a]
	18-hydroxystearic	96.6–97.2[19]	*erythro*-11,12-dihydroxystearic	129–130[62a]
			threo-12,13-dihydroxystearic	95.5–97[62a]
			erythro-12,13-dihydroxystearic	125[p]
(19)	2-hydroxynonadecanoic	93	dihydroxyjecoleic	128
	4-hydroxynonadecanoic	?		
	19-hydroxynonadecanoic	91–91.5[19]		
(20)	2-hydroxyarachidic	94, 91–92[o]	*threo*-9,10-dihydroxyeicosanoic	97–98[bb]
	3-hydroxyarachidic	92	*erythro*-9,10-dihydroxyeicosanoic (dihydroxygadoleinic)	130.1[oo]
	4-hydroxyarachidic	54–55(lactone)		
	20-hydroxyarachidic	97.4–97.8[19]	*threo*-11,12-dihydroxyeicosanoic	94–95[109]
			erythro-11,12-dihydroxyeicosanoic	130.5[q]
			13,14-dihydroxyeicosanoic	98–99[75]
(21)	2-hydroxyheneicosanoic	96, 93–94[62]		
	21-hydroxyheneicosanoic	92.5–93[19]		

TABLE 15 (*continued*)

Total Carbons	Monohydroxy Acids $C_nH_m(OH)\cdot COOH$	M.P. (°C)	Dihydroxy Acids $C_nH_{m-1}(OH)_2COOH$	M.P. (°C)
(22)	2-hydroxybehenic	96.5	*erythro*-2,3-dihydroxybehenic	132–133
	3-hydroxybehenic	95?		
	4-hydroxybehenic	34		
	13-hydroxybehenic	88–91[23], 87–87.5[23a], 74–76 (f.p.)[22]	*threo*-13,14-dihydroxybehenic	100[43], 98–99[40]
			erythro-13,14-dihydroxybehenic	130.4[m], 128[43]
	14-hydroxybehenic	90[23a]		
	22-hydroxybehenic (phellonic of Jensen)	99.6[a]		
(24)	2-hydroxylignoceric (cerebronic of Klenk)	97.3[y], 93–95[141], 92 (f.p.)[w], 101[r]		
	4-hydroxylignoceric	68 (lactone)		
	22-hydroxylignoceric	93–93.5 (f.p.)[20]		
(25)	2-hydroxypentacosanoic	102–104[14]		
	8-hydroxypentacosanoic (cerebronic of Brigl)	101–102		
(26)	2-hydroxycerotic	101.6, 101–103.5[119]		
	4-hydroxycerotic			
(28)	2-hydroxyoctacosanoic	104		
(30)	2-hydroxymelissic	106, 97.5[118]	*threo*-dihydroxymelissic (lanoceric)	104–105
	4-hydroxymelissic	88 (lactone)	*erythro*-dihydroxymelissic	102.5[54a] 140
(31)	2-hydroxyuntriacontanoic (coccceric)	110		
(32)	2-hydroxydotriacontanoic	108		
(33)	2-hydroxytritriacontanoic	11?		
	33-hydroxytritriacontanoic (pemphygic)	101–102		
(34)	2-hydroxytetratriacontanoic	109–110 (B-form)		

3-hydroxy acids with odd number of 13 or more carbons if formed are unstable and revert to the corresponding γ-monoethylenic acids. The 34-α-hydroxy acid crystallizes from benzene with a melting point of 109–110°C (B-form), but on solidification melts at 104–105°C (C-form). The B-form or unstable modification has a crystal spacing of 80.5 Å, whereas the C-form gives the value 73.3 Å. The naturally occurring 16-hydroxypalmitic (*juniperic*) acid in coniferous waxes melts at 95°C, but the melting point decreases to 83°C if heated for a short time.

TABLE 15 (*continued*)

[a]mean of m.pt. 59–60 by Asaño[4]; [b]av. of 51–51.5[19], 53–54[80] m.pts.; [c]av. of 119–121[12], 118–118.5[42] m.pts.; [d]av. of 75[51], 75.5–76.5[10] m.pts.; [e]av. of 70–70.5[19], 65.8[80] m.pts.; [f]av. of 84–85[19], 84[118], 83–84[80], 84[111b] m.pts.; [g]av. of 83[48], 89.5, 87[96], 89–90[108] m.pts.; [h]av. of 123–124[48], 124.5, 125[96] m.pts.; [i]av. of 95[19], 91[121], 92–93[69], 93–94[138], 95[11a] m.pts.; [j]av. of 81–82[97], 73[25], 81.5[143] m.pts.; [k]av. of 95[96], 93–94[62a, 151], 94–95[60], m.pts.; [l]av. of 132.6, 132[98, 125], 137[121], 130–131[151], 131[48], 129–131[62a] m.pts.; [m]av. of 128[48], 133[96], 130–130.6[69], m.pts.; [n]from plant origin[141]; [o]by Baczewski (1896); [p]av. of 126, 129.5[97], 119–120[62a] m.pts.; [q]by Green, Hilditch and Stainsby (1936); [r]by Klenk (1928)[70]; [s]by Brooks and Humphrey (1918); [t]by Chittenden and Smith (1884); [u]by Pigulevskii and Simonova, cf. C.A. 34, 4381 (1940); [v]by Kawasaki (1950), cf. C.A., 45, 5624; [w]by Meyer, Brod and Soyka[100]; [x]by Levene and Taylor (1922); [y]av. of 98.5, 94–95[b], 98.6–99.2[88a] m.pts.; [z]av. of 98–99[60, 101], 100[48, 96], 99.3–99.6[56b]; [aa]by Hergert and Kurth (1952); [bb]by Broughton *et al.* (1952)[14a]; [cc]av. of 127.5–128, 132, 130–131[14a].

designated as β and α forms. Tetrahydroxy stearic acid has α, β (*trans* addition products), and γ, δ (*cis* addition products) forms.

stearic, m.p. 69.6°C 9-hydroxystearic, m.p. 74.5°C 9,10-dihydroxystearic, m.p. 98°(*cis*), 132°C (*trans*) trihydroxystearic, m.p. 110.5°C (β), 141°C (α)[48] tetrahydroxystearic (sativic), m.p. 163.5°C (β), 173°C (α)[48] hexahydroxystearic (linusic), m.p. 169°C (β), 203°C (α)

Both dihydroxystearic acids (m. 133 and 98°C),

$$CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_7\,CO_2H$$

yield estolides on heating to 200°C. At 300°C they split into hydroxystearic acid and ι-hydroxyoleic acid, which as enol rearranges to form ι-ketostearic acid (m. 83°C).

The solubilities of the α- β dihydroxy acids at 20°C as given by Breusch and Tulus[12] are as follows:

Chain Length	Water	Ethyl Ether	Alcohol
C_9	0.54	2.2	25.2
C_{10}	0.09	1.7	16.8
C_{11}	0.003	1.2	10.5
C_{12}	0.007	0.95	7.7
C_{14}	0.006	0.72	3.4

An example of a trihydroxy acid found in nature is *β-aleuritic acid* (m. 99–100°C), a minor constituent of shellac wax, but a major one in shellac resin. Aleuritic acid corresponds to 9,10,16-*trihydroxypalmitic acid*,[107, 108] $HOCH_2(CH_2)_5CH(OH)CH(OH)(CH_2)_7CO_2H$.

It can be obtained in 14 per cent yield by the saponification of shellac with 5 per cent *N* sodium hydroxide at room temperature. When aleuritic acid is heated above its melting point, after 10 hours at 150°C, it yields a waxy, white, opaque polymer (m. 60–68°C). If it is heated longer the melt-

ing point increases, because of the formation of a linear polyester involving the COOH and ω-HO groups.

Sativic acid, a constituent of several bark waxes, may occur in the α,β tetrahydroxystearic acid form, when it will have a depressed melting point of 157–159°C.

Lactone Formation. A characteristic reaction of acids containing a double union or an OH in the γ position is that of lactone formation—a cyclization or intraesterification reaction which may involve one or more molecules. The γ- and δ-hydroxy acids lose a mol of water at ordinary temperatures, and change into γ- and δ-lactones, which are simple cyclic esters that carry a methylene side chain. For example,

$$Me(CH_2)_{17}\cdot CHOH\cdot CH_2\cdot CH_2\cdot COOH \rightleftarrows Me(CH_2)_{17}\cdot CH\cdot CH_2\cdot CH_2\cdot CO + H_2O$$

γ-hydroxybehenic acid — *γ-behenolactone*

The ease of lactone formation varies greatly with the position of the OH group in the polymethylene chain; the γ- and δ-hydroxy acids exhibit so marked a tendency toward lactone formation that the free acid with OH in the 4- or 5- position is frequently difficult to obtain. The γ- and δ-lactones are the most stable; α- and β-OH-acids do not ordinarily form lactones. Lactonization is an equilibrium reaction; the equilibrium mixture generally contains 30 to 60 per cent of lactone, and the degree of cyclization, or yield of monomeric lactone, varies inversely as the concentration of the hydroxy acid. Unsaturated acids in which the double union occurs in the β,γ or γ,δ position yield lactones by heat alone.[154] In the case of acids having the OH or double union further than the γ-position, the formation of lactones may be preceded by migration of the OH or double union to the γ-position. β-hydroxy acids on dehydration give α,β-unsaturated acids rather than β-lactones; α-lactones are not known, but cyclic intermolecular esters (dilactones or lactides) are formed from two molecules of an α-hydroxy acid by heating.

The γ-saturated lactones of the higher fatty acids are solid, e.g., *γ-myristolactone* (m. 29°C, 30–31°C)[122]; *γ-palmitolactone* (m. 41°C)[62]; *δ-palmitolactone* (m. 29.5–30.0°C); *γ-stearolactone* (m. 47.5°C); *γ-behenolactone*, $C_{22}H_{42}O_2$, which when prepared from erucic acid is in the form of glittering leaflets (m. 63.5°C)[154]; and *γ-lignocerolactone*, $C_{24}H_{46}O_2$ (m. 68°C). The C_{26} lactone (*cerotolactone*) melts at 76°C, and a C_{30} lactone (*myricinolactone*) melts at 88°C. The latter is a constituent of candelilla wax. γ-Myristolactone is an accredited constituent of beeswax. The series of solid γ lactones with an odd number of carbons begins with tridecalactone ($b_{9.5}$ 178–180°C, d^{15} 0.9327, m. 17–18°C). They are not constituents of waxes.

γ-Lactones can be prepared from γ-keto acids by treatment with sodium amalgam in aqueous alkali, and the γ-hydroxy acid from γ-lactone by refluxing with an excess of NaOH and then acidifying with HCl. However, the hydroxy acid, if refluxed with 15 per cent HCl, will again yield γ-lactone[62]. γ-ketopalmitic acid (m. 91.5–92.5°C) yields γ-palmitolactone (m. 40.7–41.3°C), which yields reversibly γ-hydroxypalmitic acid (m. 79–79.6°C)[62].

Lactones of the shorter chain length like butyrolactone are fragrant. Anolides such as 1,4-undecanolide ($C_{11}H_{20}O_2$, b_{13} 162°C) has a strong peach-like odor; α-substituted γ-butyrolactones are particularly fragrant.

The ω-1-lactones occur in nature in dimeric and trimeric as well as in monomeric form. The lower ω-hydroxy acids form chiefly monomeric lactones, whereas the higher ones tend to yield mixed dimeric and trimeric lactones, although increasing temperature and concentration of the hydroxy acid favor formation of lactones of the monomeric type. When the ω-lactones are prepared synthetically from their corresponding ω-hydroxy acids, as by heating in the presence of benzenesulfonic acid, both monomeric and dimeric lactones are formed.

Cyclization or lactone ring formation should be distinguished from the so-called etholide formation, which essentially is a linear esterification resulting in simple or polyetholides. Etholides combine the properties of alcohols, acids, and esters, which is not true of the cyclized lactones.

Polymethylene Acid Alcohols. Hydroxy acids which have an OH end group such as 9-hydroxynonanoic acid, $CH_2(OH)(CH_2)_7 \cdot COOH$, have both alcoholic and acidic properties. They are condensable in open chain formation to etholides, in which the respective terminal groups of OH and COOH combine with the elimination of H_2O, much in the same manner as in the formation of esters[11b]. For example, the simple etholide formed from 9-hydroxynonanoic acid is:

$$CH_2(OH)(CH_2)_7CO_2 \cdot CH_2(CH_2)_7 \cdot COOH \text{ (m. 60–61°C)}^{19}$$

When heated at 200°C for 1 hour the C_{18} etholide couples to form a double etholide (C_{36})[19]:

$$HO_2CH(CH_2)_7CH_2 \cdot O_2C(CH_2)_7CH_2 \cdot O_2C(CH_2)_7CH_2 \cdot O_2C(CH_2)_7 \cdot CH_2OH$$

(m. 71–72°C)

A C_{20} double etholide melts at 56–56.5°C; the triple etholide at 72.5–73°C.

Etholides and polyetholides (estolides) are constituents of waxes derived from plants and conifers. Instead of a linear esterification, ring closures may take place, resulting in ω-1-lactones of the anolide class. A pure lactone of 15-hydroxypalmitic acid (juniperinic acid) melts at 15°C (d^{33} 0.9397, acid no. 1.5, ester no. 226.8)[128], whereas the 16-hydroxypalmitic acid yields

an anolide; 16,1-hexadecanolide, when synthesized in macrocyclic but monomeric ring formation by Hunsdiecker and Erlbach[63], melted at 36°C.

Cyclization of ω-Br aliphatic acids by boiling dilute solutions of methyl ethyl ketone with an excess of potassium carbonate, using the so-called dilution principle, gave lactone yields of 84–95 per cent from dodecanolide upward. These investigators reported yields, melting and boiling points, and densities of these lactones in a series ranging from C_9 to C_{17}[63].

Anolide Ring Closures. The anolide ring closures of ω-hydroxy acids have appreciably lower melting points than the etholides (also see waxes of conifers, p. 246).

Solid Monocyclic Lactones of Even Carbon Chain

		M.P. (°C)	B.P. (°C)
C_{14}	14,1-tetradecanolide	33–33.7[61]	135/3.5 mm[63]
C_{16}	16,1-hexadecanolide	35.5–36.5[63]	128/1.0 mm[63]
C_{18}	18,1-octadecanolide	36–37[139]	136–8/0.15 mm

The solid ω-1-lactones (cyclized) or anolides of odd carbon chain have boiling and melting points (°C) as follows[63]: 9,1-nona-anolide b_{13} 93, m. 31–31.5 (24–26.5)[139]; 13,1-tridecanolide $b_{3.8}$ 122, m. 27.5; 15,1-pentadecanolide b_2 127, m. 37–37.5; 17,1-heptadecanolide, $b_{2.8}$ 155, m. 42–43; 23,1-tricosanolide m. 35–36.

The solid dimeric cyclized lactones of ω-hydroxy acids of even carbon chain have the following melting points (°C)[129]: C_8 92.5–93.5; C_{10} 96–97; C_{12} 100–101; C_{14} 106–107; C_{16} 108–109[129]; C_{18} 113–114.

The solid trimeric cyclized lactones of ω-hydroxy acids have the following melting points (°C)[129]: C_{10} 28–29; C_{15} 70–72.

Wax Esters

Esters resulting from the union of the higher fatty acids with higher aliphatic alcohols, and less often with the cyclic alcohols such as the sterols, are the principal components of the natural animal and vegetable waxes. The higher molecular weight esters are wax-like solids. In the metabolism of the organisms of nature there appears to be a close relationship of equilibrium between acid, alcohol, ester and hydrocarbon, the latter as an end residue. Hence we may expect to encounter all four components in many of the waxes, although where there is an excess of acid constituents the percentage of free alcohols is substantially nil. When the free acid content is exceedingly low there may ocur a substantial proportion of free alcohols.

Esters are monomeric, not dimeric as are the acids and alcohols. The esters encountered in nature always have an even number of carbon atoms in chain length, although it is less certain that this rule infallibly applies for esters having an extremely high molecular weight. There is apparently

a tendency for an acid of odd carbons to combine with an alcohol of odd carbons to form an ester of an even number of carbons, e.g.,

$$C_{26}H_{53}\cdot COOH + HO\cdot C_{27}H_{55} \rightarrow C_{26}H_{53}\cdot CO\cdot OC_{27}H_{55} + H_2O$$

carbocerotic acid — *carboceryl alcohol* — *carboceryl cerotate* — *water*

A number of esters have been isolated from natural sources. Wax esters can be prepared synthetically; for example, *hexadecyl palmitate* (m. 53.5°C) has been prepared by Krafft[76] by the esterification of *n*-hexadecanol (cetyl alcohol) with palmitic acid, and also by reacting palmitoyl chloride with cetyl alcohol. The *octadecyl* ester (m. 59°C) has been prepared in a similar manner. *Octadecyl palmitate* isolated from natural sources has a somewhat lower melting point (55°C) than that of the synthetic ester. The synthesis of *docosyl behenate* (m. 75°C), and of *tetracosyl lignocerate* (m. 75.9°C) has been described; also of *hexacosyl stearate* (m. 73°C) and *triacontanyl stearate* (m. 76°C), obtained by direct esterification of their components. An x-ray examination of the crystals of *hexadecyl palmitate* reveals them to possess monoclinic symmetry. The unit cell contains two double molecules, the average C–C distance being 1.27 Å.

Melting Points of Alkyl Esters of Palmitic and Stearic Acids. Whitby[149] has given the following melting-point constants for the synthetically prepared esters of palmitic and stearic acids, except methyl esters, which are by Niemann[109] and Wagner, and the value for ·-decyl palmitate,

	M.P. (°C)	
Ester	Palmitates	Stearates
Methyl	29.0	37.0
Ethyl	23.5	33.6
Propyl	20.4	30.5
Butyl	16.9	27.5
Amyl	19.4	30.0
Iso-amyl	12.5	23.0
Octyl	22.5	31.8
Decyl	30.0	—
Cetyl	51.6	56.5

It will be noted that the melting points of the alkyl esters of the same acyl radical decrease somewhat as the alkyl group lengthens from 1 to 8 carbons, after which they increase. The melting points rise with an increase of acyl carbon atoms in the wax acids. For example, *methyl stearate* melts at 37°C, and *methyl montanate* at 66°C; *ethyl montanate* melts at 64–65°C, but *propyl montanate* melts at 63.5°C.

Methyl montanate may be prepared by boiling montanic acid with

methanol in the presence of sulfuric acid. The resulting montanate can be crystallized in the form of curved needles.

Lower Alkyl Esters of Wax Acids. The melting points and other constants of the lower alkyl esters—methyl, ethyl, propyl, butyl—are helpful in identifying the acids esterified. These esters are never found as components of waxes. Levene and Taylor[83] considered the published melting points of the methyl and ethyl esters of the higher fatty acids a trifle low, and in 1924 established new ones from synthetically prepared esters (C_{16} to C_{28}). Most of the melting points of Levene and Taylor are given in ranges with a spread of 1 degree. In 1930 Francis and Piper reported precise constants of setting point, resolidification point, and melting point for the esters of most of the higher fatty and wax acids. Table 16 is based in part upon their figures and upon more recent ones of Jones[67], and values given by Monick[102] for the C_{12}, C_{14}, C_{16}, C_{18} acids as methyl esters.

The melting points of methyl esters are given here in the β form, a stable polymorphic form crystallized from the melt before the temperature has fallen more than 1°C; those of ethyl esters are given in the α form as crystallized from ethanol. In the methyl esters, the β-esters are those with the lower melting points. In Table 16 the melting points of the esters that have an odd number of carbon atoms in the acyl radical are staggered from those of an even number of carbons, since they fall on slightly different curves when plotted.

It is of interest to note that the boiling points of the esters fall in line, irrespective of whether the number of carbons is even or odd, which is, of course, not true of the melting points. It will be observed in Table 16 that the melting and boiling points of the methyl esters are somewhat higher than those of the corresponding ethyl esters.

Refractive indices at 45°C of the methyl esters of C_{12}, C_{14}, C_{16} and C_{18} acids by Monick[102] are 1.4215, 1.4271, 1.4317, and 1.4346, respectively. These values differ somewhat from those determined by Wyman and Barkenbus[152], which agree well with those of Krewson[75b].

The saponification numbers of the methyl esters of C_{12}, C_{14}, C_{16} and C_{18} acids have been given by Monick[102] as 26.17, 23.14, 20.74 and 18.79 respectively. The interplanar x-ray crystal spacings of the alkyl esters show chain lengths which are monomolecular. This makes it possible to purify the wax acids by preparing their ethyl and other alkyl esters, then separating the esters by fractional distillation or by crystallization.

Higher alkyl esters, such as the higher cetyl esters, can be synthesized in the following manner: equimolar amounts of stearic acid and cetyl alcohol are mixed at atmospheric pressure, and a current of carbon dioxide is passed through the mixture. The reaction begins at 220°C and is complete in two hours. The temperature is increased to 270°C to secure a 95 per cent yield of *cetyl stearate*.

TABLE 16. ALKYL ESTERS OF HIGHER FATTY AND WAX ACIDS

Acyl Carbons	Acid	(Methyl Ester β form)		Ethyl Ester (α form)	
		M.P. (°C)	B.P. (°C)	M.P. (°C)	B.P. (°C)
12	Lauric	5.0[m]	113/4 mm[m]		
14	Myristic	18.8[p], 19.0[n]	141/4 mm	11.9, 4.5 (f.p.)[q]	
16	Palmitic	29.5[n], 30.4[w]	163/4 mm	23.5[n], 19.4 (f.p.)[f, q]	185/10 mm
17	Margaric	28.6[p]	170/1 mm	25.7	—
18	Stearic	38.7[p], 38.0	184/4 mm[m]	31.4[p], 33.6[n], 32[f]	152/0.18 mm
19	Nonadecylic	38.9[p]	100/3.75 mm[u]	36.1[p]	167/0.27 mm
20	Arachidic	45.8[p], 46.5[r, w]	206.5/5 mm	40.5[f, p] 42.0[r]	177/0.28 mm
21	Medullic	47.2[p]	207/3.75mm[u]	44.5[p]	185/0.20 mm
22	Behenic	52.7[p], 53.2[w]	224/5 mm	48.3[p, s] 48.7[f]	192/0.22 mm
23	Tricosoic	54.0[p]	—	51.4[p]	199/0.27 mm[l]
24	Lignoceric	57.8[p], 59.7[v]	242/5 mm	54.4[p], 54.7[f, s]	208/0.24 mm
25	Pentacosic	59.5[p]	—	57.1[p]	217/0.5 mm[l]
26	Cerotic	62.9, 63.8[w]	258/5 mm	60.2[f], 59.7[s]	199/0.30 mm
27	Heptacosoic	65.0	266/5 mm	61.5	
28	Montanic	66.7[p], 68.5[w]	270/5 mm	64.6[f, p] 64.9[s]	
29	Nonacosoic	68.8	277/5 mm	66.6[f, p]	
30	Myricinic (*n*-Melissic)	70.8[p], 71.5	282/5 mm	68.5[f, p] 70.5[k]	
31	Hentriacontanoic	70.2[j]	—	69.0	—
32	Lacceroic	74.1[p]	—	72.5[f, p]	—
33	Tritriacontanoic	75.2[j], 76.5[k]	—	70.2[j], 75[k]	—
34	Geddic	77.2[p]	—	75.4[f, p]	—
35	Ceroplastic	75.9[j], 79[k]	—	77.7[k], 73.2[j]	—
36	Hexatriacontanoic	80.3[p]	—	78.6[f, p]	
37	Heptatriacontanoic	—	—	75.9[j]	
38	Octatriacontanoic	82.7[p]	—	80.6[f, p]	
46	Hexatetracontanoic	91.4[p]		90.5[f] (β form)	

[f] Francis *et al.*[33]; [j]Jones[67]; [k]Kono; [m]Monick[102]; [l]Levene and Taylor[85]; [p]Francis and Piper[35]; [q]Malkin[93]; [n]Whitby; [r]mean melting point values of Adam and Dyer[1]; [s]Bleyberg and Ulrich[10]; [t]Mrs. Robinson[121]; [u]Cason *et al.* (1951); [v]Meyer, Brod and Soyka[100]; [w]Krewson[78b].

TABLE 17. INDICES OF REFRACTION (n^t) FOR METHYL ESTERS OF C_8–C_{32} *n*-ALIPHATIC ACIDS

	M.P. (°C)[75b]	n^{45} [152]	n^{50} [75b]	n^{80} [75b]
Methyl caprylate		1.4069	—	—
Methyl caprate		1.4161	—	—
Methyl laurate		1.4220	1.4199	1.4078
Methyl myristate		1.4281	1.4249	1.4131
Methyl palmitate	30.4	1.4317	1.4294	1.4173
Methyl stearate	39.0	1.4346	1.4328	1.4213
Methyl arachidate	46.5	—	1.4352	1.4238
Methyl behenate	53.2	—	—	1.4262
Methyl lignocerate	59.2	—	—	1.4283
Methyl cerotate	63.8	—	—	1.4301
Methyl montanate	68.5, 67.4[88a]	—	—	1.4320

Note: Wyman and Barkenbus[152] state that the methyl stearate was fractionated through a 10-plate Podbielniak column; methyl esters of caprylic, capric, lauric, and myristic through the spinning-band type of column.

Hydroxyl Alkyl Ester Polymers. The various polyesters, which result from the interesterification of the terminal aliphatic hydroxy acids, such as the etholides and polyetholides found in nature, can be prepared synthetically. In fact they can be prepared with much greater molecular weights, ranging from 1000 to 9000 or more. A good example is *ω-hydroxydecanoic* (*10-hydroxycapric*) acid, which when heated in either the presence or absence of a catalyst produces a chain polyester of the formula.

$$HO(CH_2)_9CO_2[(CH_2)_9CO_2]_n\cdot(CH_2)_9CO_2H$$

Prolonged heating results in polyesters, which are tough, opaque solids capable of being drawn into threads. Carothers and Van Natta[16b] prepared polyesters from ω-hydroxydecanoic acid which range in molecular weight from 780 to 25,200. Strong, oriented fibers are obtained from a polyester of a molecular weight of 17,000 more or less. The melting points of the polyesters vary from 66–67 to 75–80°C, the densities (d_4^{25}) 1.0957 to 1.0621, and the refractive indices (n_D^{25}) from 1.4494 to 1.4515.

The ω-polyester from ω-hydroxypentadecanoic acid can be prepared by heating the acid in a molecular still under high vacuum, or in a vessel with a stream of inert gas. The product resulting from a 7 days' reaction at 95°C is a stiff transparent mass which holds its shape up to 200°C and can be drawn into fibers, or cold-drawn[16a].

Glycerides

The natural glycerides are generally highly mixed. Simple triglycerides appear to be the exception rather than the rule. Each of the individual fatty acids of a fat tends to be apportioned as evenly as possible among the different glyceride molecules. For example, the component acids of the glycerides of cocoa butter are stearic-oleic-oleic (12 per cent), palmitic-

TABLE 18. SIMPLE ALIPHATIC ESTERS OCCURRING IN NATURAL WAXES

Ester	$C_mH_{2m}O_2$ Carbon No.		M.P. (°C)	Molecular Weight
	Acyl R	Alkyl R		
Cetyl laurate[c]	C_{12}	C_{16}	41(C)	424.73
Myristyl myristate	C_{14}	C_{14}	38, 43	424.73
Cetyl myristate[c]	C_{14}	C_{16}	47(R), 48(C)	452.78
Stearyl myristate	C_{14}	C_{18}	52	480.83
Ceryl myristate	C_{14}	C_{26}	62[a]	593.04
Cetyl palmitate[c, d]	C_{16}	C_{16}	51.6(W) 53.5(K)[a]	480.83
Octadecyl palmitate	C_{16}	C_{18}	55	508.88
Arachyl palmitate	C_{16}	C_{20}	56	536.93
Behenyl palmitate	C_{16}	C_{22}	60	564.99
Lignoceryl palmitate	C_{16}	C_{24}	65	593.04
Ceryl palmitate[c, h, i, j]	C_{16}	C_{26}	69	621.09
Myricyl palmitate[c, i]	C_{16}	C_{30}	73a[a], 72	677.20
Lacceryl palmitate[c]	C_{16}	C_{32}	75	705.25
Octadecyl stearate	C_{18}	C_{18}	58.5(S), 62(SA)	536.93
Cetyl stearate	C_{18}	C_{16}	55, 56.5(W)	508.88
Ceryl stearate[i]	C_{18}	C_{26}	73(G)	649.14
Myricyl stearate	C_{18}	C_{30}	76(G)	705.25
Ceryl arachidate	C_{20}	C_{26}	74	677.20
Docosyl behenate	C_{22}	C_{22}	75[a]	649.14
Ceryl behenate	C_{22}	C_{26}	80	705.25
Carnaubyl isobehenate	C_{22}	C_{24}	78.5	677.20
Myricyl isobehenate[b]	C_{22}	C_{30}	82	761.35
Tetracosyl lignocerate	C_{24}	C_{24}	75.9[a]	705.25
Ceryl lignocerate[k, m]	C_{24}	C_{26}	79	733.30
Montanyl lignocerate[k]	C_{24}	C_{28}	81	761.35
Ceryl carnaubate[m]	C_{24}	C_{26}	78.5	733.30
Myricyl lignocerate[b, l, k]	C_{24}	C_{30}	83	789.40
Ceryl cerotate[k, l, m]	C_{26}	C_{26}	81(D), 75.5(Ky)	761.35
Montanyl cerotate	C_{26}	C_{28}	83.5	789.40
Myricyl cerotate[l, l]	C_{26}	C_{30}	87	817.46
Lacceryl cerotate	C_{26}	C_{32}	89	845.51
Carbоceryl methylhexacosanate	C_{27}	C_{27}	82(Ky), 84(G)	789.40
Melissyl isoheptacosanate	C_{27}	C_{31}	86(Ky)	845.51
Montanyl montanate	C_{28}	C_{28}	85, 89	817.46
Myricyl montanate	C_{28}	C_{30}	87, 86	845.51
Melissyl methyloctacosanate	C_{29}	C_{31}	91	873.55
Myricyl triacontanate	C_{30}	C_{30}	91.5, 90.3	873.55
Lacceryl triacontanate	C_{30}	C_{32}	93	901.60
Geddyl triacontanate	C_{30}	C_{34}	94	939.65
Melissyl melissate	C_{31}	C_{31}	92.5, 90.5(G)	901.60
Lacceryl lacceroate[m]	C_{32}	C_{32}	92.5, 95(G)	939.65
Geddyl lacceroate	C_{32}	C_{34}	98	957.72

TABLE 18 (*continued*)

[a] Synthetic; [b]constituent of corn wax, [c]of spermoil, [d]of spermaceti, [e]of beeswax, [f]of bark wax of privet tree, [g]of latex-bearing plants, [h]of wax of indigo plant, [i]of wax of ceanothus plants, [j]of rice-oil wax, [k]of Chinese insect wax, [l]of carnauba wax, [m]of shellac wax, [n]of montan wax.

[y] C_{2n} may be regarded as the total number of C atoms, that is, the sum of the carbons in the acyl and alkyl radicals of the alkyl ester.

(C)—Cataline, (D)—Damoy, (G)—Gascard, (Ky)—Koyama, (R)—Rheinboldt[115b], (S)—Shinosaki, (SA)—Sauer and Adkins[128a], (W)—Whitby,[149] (K)—Krafft

palmitic-stearic (2.5 per cent), etc. These triglyceride acids are roughly grouped as trisaturated, disaturated and monosaturated. Cocoa butter contains 2.5 per cent trisaturated, 76.8 per cent disaturated, and 20.7 per cent monosaturated triglycerides. The melting points (α form) of the triglycerides of even number of carbons are as follows (°C): C_{10} 18, C_{12} 14, C_{14} 32, C_{16} 44, C_{18} 54. The melting points (β form) of the same triglycerides are (°C): C_{10} 31.5, C_{12} 43.9, C_{14} 55.5, C_{16} 65.5, C_{18} 73.1.

Triglycerides. The melting points of many of the saturated fatty acids are in close proximity, or slightly higher, than those of the corresponding triglycerides, for acids having 10 or more carbon atoms. This is shown in the following data:

		Triglycerides (β form-inclined chains		
Fatty Acids	M.P. (°C)		M.P. (°C)	Long crystal x-ray spacing (Å)
Caproic	−8.0	Caproin	−25.0	
Caprylic	16.5	Caprylin	8.1	
Capric	31.4	Caprin	31.5	26.8
Lauric	43.8	Laurin	46.4	31.2
Myristic	53.8	Myristin	57.0	35.8
Palmitic	62.6	Palmitin	65.5	40.6
Margaric	61.3	Margarin	63.5	43.5
Stearic	69.3	Stearin	71.5	45.0
Oleic	16.3	Olein	4.9	—
Elaidic	43.7	Elaidin	41.5	44.1
Erucic	33.5	Erucin	32.5	51.1
Brassidic	64.0	Brassidin	57.0	53.6

Triple melting points (α, β, and γ) for the triglycerides are given by Clarkson and Malkin.[92a] The stable β form is associated with inclined chains, a monotropic α form with vertical chains, and a γ form is vitreous and has no long spacings. Examples of the three forms of melting point are:

	α	β (°C)	γ
Trilaurin	35.0	46.4	15.0
Trimyristin	46.5	57.0	33.0
Tripalmitin	56.0	65.5	45.0
Tristearin	65.0	71.5	54.5

TABLE 19. MOLECULAR WEIGHTS AND SAPONIFICATION VALUES OF TRIGLYCERIDES

Name	Formula	Molecular Weight	Saponification Value
Laurin	$C_3H_5(O\cdot C_{12}H_{23}O)_3$	638.98	263.41
Myristin	$C_3H_5(O\cdot C_{14}H_{27}O)_3$	723.14	232.75
Palmitin	$C_3H_5(O\cdot C_{16}H_{31}O)_3$	807.29	208.49
Hydnocarpin	$C_3H_5(O\cdot C_{16}H_{27}O)_3$	795.20	211.66
Stearin	$C_3H_5(O\cdot C_{18}H_{35}O)_3$	891.45	188.81
Olein	$C_3H_5(O\cdot C_{18}H_{33}O)_3$	885.40	190.01
Linolin	$C_3H_5(O\cdot C_{18}H_{31}O)_3$	879.35	191.40
Chaulmoogin	$C_3H_5(O\cdot C_{18}H_{31}O)_3$	879.35	190.40
Linolenin	$C_3H_5(O\cdot C_{18}H_{29}O)_3$	873.31	192.73
Clupanodonin	$C_3H_5(O\cdot C_{18}H_{27}O)_3$	867.26	194.07
Ricinolein	$C_3H_5(O\cdot C_{18}H_{33}O_2)_3$	933.40	180.32
Arachin (Arachidin)	$C_3H_5(O\cdot C_{20}H_{39}O_2)_3$	975.61	172.52
Erucin (Behenin)	$C_3H_5(O\cdot C_{22}H_{41}O)_3$	1053.71	159.73
Cerotin	$C_3H_5(O\cdot C_{26}H_{51}O)_3$	1218.07	138.18
Myricin	$C_3H_5(O\cdot C_{30}H_{59}O)_3$	1396.38	120.53
Hydroxystearin	$C_3H_5(O\cdot C_{18}H_{35}O_2)_3$	939.44	179.16
Dihydroxystearin	$C_3H_5(O\cdot C_{18}H_{35}O_3)_3$	987.44	170.45
Trihydroxystearin	$C_3H_5(O\cdot C_{18}H_{35}O_4)_3$	1035.44	162.55
Sativin	$C_3H_5(O\cdot C_{18}H_{35}O_5)_3$	1083.44	155.35
Linusin	$C_3H_5(O\cdot C_{18}H_{35}O_7)_3$	1179.44	142.70

Resins

The resins form a group of substances of very complex and variable chemical composition, but having similar physical characters. The natural resins occurs as a rule in exudations from plants, and as such are quite frequently associated with oils and waxes, that is the crude waxes derived from plant, insect, or mineral sources.

Resins may be classified as resinols (resin alcohols), resinolic or resin acids, resin-acid esters, resinol-esters, and resenes (unsaponifiable). Resenes are not alcohols or hydrocarbons (with exceptions), but chemically inert substances. Natural resins often include some resene with the resin acid.

Included in the resinols of triterpene structure are α- and β-amyrin, $C_{30}H_{49}OH$ (m. 183° and 195°C, respectively), and chironal, $C_{28}H_{47}(OH)$ (m. 173–176°C). Resinols of lower molecular weight, generally in the sesquiterpene class, are $C_{19}H_{29}(OH)$, $C_{20}H_{31}(OH)$, $C_{16}H_{25}(OH)$, $C_{14}H_{23}(OH)$, and $C_{13}H_{21}(OH)$, which are mostly liquids. Only when these resinols are oxygenated are the melting points high. For example, $C_{16}H_{25}(OH)O$, benzoresinol, melts at 274°C. Resinols which give a tannin reaction are referred to as resino-tannols, and contain from 3 to 10 oxygen atoms.

The resinolic acids of the sesquiterpene type are typified by rubeabietic acid (m. 163°C), $C_{19}H_{31}COOH$, and rubenic acid (m. 88°C), $C_{19}H_{29}COOH$, the latter ostensibly having an additional double bond. Pimaric resin

(inactive), which also has the latter formula, has a melting point of 171°C. Many of the resinolic acids encountered are oxygenated.

The acid numbers of resins are extremely variable and are notably low (15 to 81) for such resins as kauri, dammar, elemi, mastic, acroid, guaiac, etc. As a class (A) they average about 34 in acid number. Then there is a group (B) with comparatively high acid numbers, which include abietic, pimaric, sandarac, or the pine resins; these resins range from 143 to 183 in acid number and average about 157.The ester numbers of class A resins average about 54, and those of class B about 18. The iodine numbers of class A resins vary from 62 to 176, and those of class B from 91 to 138, with an average of about 120. The iodine absorption of colophony is 112 to 117. Abietic acid has a theoretical iodine absorption value of 167.9 per cent. The saponification numbers of natural resins (excluding commercial rosin) range from 21 (for elemi) to 227 (for hard Manila). The average saponification number is about 147. Rosins, however, range between 151 and 194, the average being 170.

The melting points of the resins ordinarily range between 80 and 188°C, with a mean of 134°C. Resins with more than one double bond usually melt at 43 to 91°C, e.g., resins of ponderosa pine bark crude wax melt at 82–83°C. Rosin and its derivatives, namely hydrogenated, disproportionated, and polymerized, have softening points of 83, 75, 80, and 100°C respectively, and acid values of 165, 162, 158, and 150 respectively. The chief resin acids from rosin will melt in the range of 144 to 188°C, e.g., abietic acid melts at 173–175°*B*. Oxygenated resin acids have still higher melting points, namely 188 to 248°C.

Resenes of dammar, copal, mastic, and other resinous substances have melting points which range between 62°C (in olibanum) to 206°C (in dammar). The average melting point of resenes is about 170°C.

References

1. Adam, N. K., and Dyer, J. W. W., *J. Chem. Soc.*, **127**, 70–73 (1925).
2. Adickes, F., and Andresen, G., *Ann.*, **555**, 41–56 (1943).
2a. Ames, D. E., *et al.* (Birbeck Coll. London), *J. Chem. Soc.*, **1950**, 174–177.
3. Anderson, Rudolph J., *J. Biol. Chem.*, **12**, 97–113 (1912); *ibem.*, 447–464.
3a. *Ibid.*, **17**, 141–150 (1914); *idem.*, 171–190.
4. Asano, M., *J. Pharm. Soc.* (*Japan*), No. **504**, 75–86 (1924).
5. Bagard, P., *Bull. soc. chim.*, [4], **1**, 346–365 (1907).
6. Beck, G., *Wien. Chem.-Ztg.*, **46**, 18–22 (1943).
7. Bell, H. S., "American Petroleum Refining," 2d. Ed., p. 38, New York, D. Van Nostrand Company, 1930.
8. Bergmann, W., *J. Biol. Chem.*, **104**, 553–557 (1934).
8a. ——, and Swift, A. N., *J. Org. Chem.*, **16**, 1206–1221 (1951).
9. Bernhard, K., and Albrecht, H., *Helv. Chim. Acta*, **31**, 977–988 (1948) (in German).
10. Bleyberg, W., and Ulrich, H., *Ber.*, **64B**, 2504–2513 (1931).

11. Boekenoogen, H. A., *Fette u. Seifen*, **46**, 717–719 (1939).
11a. Bougault, J., and Bourdier, L., *J. Pharm. chim.* [6], **29**, 561–573 (1909).
11b. ——, and ——, *Compt. rend.*, **147**, 1311–1313 (1908).
12. Breusch, F. L., and Tulus, R., *Rev. faculté sci. univ. Istanbul*, **12A**, 289–293 (1947) (in German).
13. ——, and Keskin, H., *Arch. Biochem.*, **18**, 305–318 (1948).
14. Brigl, Percy, *Z. physiol. Chem.*, **95**, 161–194 (1915).
14a. Broughton, B. W., *et al.*, *J. Chem. Soc.*, **1952**, 671–677.
15. Calvin, M., and Benson, A. A., *Science*, **109**, 140–142 (1949).
16. Carothers, W. H., *et al.*, *J. Am. Chem. Soc.*, **52**, 5279–5288 (1930).
16a. ——, and Hill, J. W., *J. Am. Chem. Soc.*, **54**, 1559–1566 (1932).
16b. ——, and Van Natta, F. J., *J. Am. Chem. Soc.*, **55**, 4714–4719 (1933).
17. Cason, J., *J. Am. Chem. Soc.*, **64**, 1106–1110 (1942).
17a. ——, and Prout, F. S., *J. Am. Chem. Soc.*, **66**, 46–50 (1944).
17b. ——, and Adams, C. E., *et al.*, *J. Am. Chem. Soc.*, **66**, 1764–1767 (1944).
18. ——, *et al.*, *J. Org. Chem.*, **15**, 135–138 (1950); *ibid.*, 139–148 (1950).
18a. Cavanna, R., and Ställberg-Stenhagen, S., *Ricerca sci.*, **20**, 1709–1710 (1950).
18b. ——, and ——, *Atti. accad. nazl. Lincei. Mem. classe sci. fis. mat. e nat.* [8], **3**, No. 2, 31–42 (1950).
19. Chuit, P., and Hausser, J., *Helv. Chim. Acta*, **12**, 463–492 (1929).
19a. ——, *ibid.*, **9**, 264–278 (1926).
20. ——, *et al.*, *ibid.*, **9**, 1074–1093 (1926).
21. ——, *ibid.*, **10**, 113–131 (1927).
22. Clarke, E. W., *Ind. & Eng. Chem.*, **43**, 2526–2535 (1951).
23. Clarkson, C. E., and Malkin, T., *J. Chem. Soc.*, **1934**, 666–671.
24. Cohen, N. H., Lab. chim. org., Univ. Utrecht, *Rec. trav. chim.*, **28**, 368–390 (1909); *idem.*, 391–394.
25. D'Ambrosio, A., *Ann. chim. applicata*, **16**, 443–451 (1928); [*Chem. Abstracts*, **21**, 893 (1927).]
25a. Damoy, G., *J. pharm. chim.*, **29**, 148–158, 225–236 (1924).
26. David, S., *Bull. soc. chim. France*, **1949**, 155–160.
27. Davies, L. A., and Adams, Roger, *J. Am. Chem. Soc.*, **50**, 1749–1755 (1928).
28. Deffet, L., *Bull. soc. chim. Belg.*, **49**, 385–402 (1931).
28a. Delcourt, Mlle. Y., *Bull. soc. chim. Belg.*, **40**, 284–294 (1931).
29. Dorinson, A., and McCorkle, M. R., and Ralston, A. W., *J. Am. Chem. Soc.*, **64**, 2739–2741 (1942).
30. Drake, N. L., Carhart, H. W., and Mozingo, R., *J. Am. Chem. Soc.*, **63**, 617–620 (1941).
31. Deuel, Jr., H. J., "The Lipids, their Chemistry and Biochemistry, Volume 1: Chemistry," New York, Interscience Publishers, Inc., 1951.
32. Epifanov, F., *J. Russ. Phys. Chem. Soc.*, **40**, 133–139 (1908).
33. Fairweather, D. A., *Proc. Roy. Soc. Edinburgh*, **45**, 283–285 (1925).
34. ——, *Phil. Mag.* [7], **1**, 944–950 (1926).
34a. Findley, T. W., and Brown, J. B., *J. Am. Oil Chem. Soc.*, **30**, 291–298 (1953).
35. Fieser, L. F., and Szmuszkovics, J., *J. Am. Chem. Soc.*, **70**, 3352–3355 (1948).
36. Flaschenträger, B., and Halle, F., *Z. physiol. Chem.*, **190**, 120–140 (1930).
37. Fordyce, C. R., and Johnson, J. R., *J. Am. Chem. Soc.*, **55**, 3368–3372 (1933).
38. Francis, F., Collins, F. J. E., and Piper, S. H., *Pro. Roy. Soc.* (*London*), **A168**, 691–718 (1937).
39. ——, and Piper, S. H., *J. Am. Chem. Soc.*, **61**, 577–581 (1939).
40. ——, King, A. M., and Willis, J. A. V., *J. Chem. Soc.*, **1937**, 999–1004.

41. ——, Piper, S. H., and Malkin, T., *Pro. Roy. Soc.* (*London*), **A128**, 214–252 (1930).
43. Garner, W. E., and Ryder, E. A., *J. Chem. Soc.*, **127**, 720–730 (1925).
44. ——, *et al.*, *ibid.*, **1931**, 1533–1534.
45. Gascard, A., *Ann. chim.* [9], **15**, 332–389 (1921).
46. ——, *Compt. rend.*, **170**, 886–888 (1920); *idem.*, 1326–1328.
47. Gottfried, A., and Ulzer, F., *Chem. Umschau Fette, Oele, Wachse u. Harze*, **33**, 141–145 (1926).
48. Green, T. G., and Hilditch, T. P., *J. Chem. Soc.*, **1937**, 764–767.
49. Grün, A., *Ber.*, **39**, 4400–4408 (1906).
50. ——, and Czerny, W., *Ber.* **59B**, 54–63 (1926).
51. ——, and Wirth, T., *Ber.*, **55B**, 2206–2218 (1922).
52. ——, and Wittka, F., *Chem. Umschau Fette, Oele, Wachse u. Harze*, **32**, 257–259 (1925).
53. Heiduschka, A., and Gareis, M., *J. prakt. Chem.*, **99**, 293–311 (1919).
54. ——, and Nier, E., *ibid.* [2] **149**, 98 (1937).
55. Hendricks, S. B., *Chem. Revs.*, **7**, 431–477 (1930).
56. Hildebrand, J. H., and Wachter, A., *J. Am. Chem. Soc.*, **51**, 2487–2488 (1929).
57. Hilditch, T. P., "Industrial Chemistry of the Fats and Waxes," Covent Garden, WC2, London, Bailliere, Tindall, and Cox, 1927.
58. Holde, D., and Bleyberg, W., *Metallborse*, **20**, 1855–1856 (1930).
58a. ——, *Z. angew. Chem.*, **43**, 897–902 (1930).
59. Holde, D., and Gentner, R., *Ber.*, **58B**, 1418–1424 (1925).
60. Hopkins, C. Y., *Can. J. Research*, **24B**, 211–220 (1946).
61. ——, *et al.*, *ibid.*, **27B**, 35–41 (1949).
62. Houston, D. F., *J. Am. Chem. Soc.*, **69**, 517 (1947).
62a. Huber, W. F., *J. Am. Chem. Soc.*, **73**, 2730–2733 (1951).
63. Hunsdiecker, H., and Erlbach, H., *Chem. Ber.*, **80**, 129–137 (1947).
64. Ichiba, A., *Sci. Papers Inst. Chem. Research* (*Tokyo*), **28**, 112–123 (1935).
65. Jacini, G., *Gazz. Chim. ital.*, **77**, 247–251 (1947).
65a. Jamieson, G. S., "Vegetable Fats and Oils," 2d. Ed., New York, Reinhold Publishing Corp., 1943.
66. Jonas, K. G., *Papier-Fabr.*, **26**, 221–229 (1928).
67. Jones, R. G., *J. Am. Chem. Soc.*, **69**, 2350–2354 (1947).
68. Kerschbaum, M., *Ber.*, **60B**, 902–909 (1927).
69. Kiesel, A., *Ber.*, **58B**, 1986–1988 (1925).
70. Klenk, E., *Z. physiol. Chem.*, **166**, 287–293 (1927); *ibid.* **174**, 214–232 (1928).
71. Komori, S., and Ueno, S., *Bull. Chem. Soc. Japan*, **10**, 1128–1133 (1934); *ibid.*, **12**, 226 (1937).
72. Kono, M., and Maruyama, R., *J. Agr. Chem. Soc. Japan*, **10**, 1228–1235 (1934); *ibid.*, **12**, 523–530 (1936).
73. Kozlov, N. S., *Neftyanoe Khoz.*, **26**, 47–51 (1948).
74. Krafft, F., *Ber.*, **11**, 2218 (1878).
75. ——, *Ber.*, **1882**, 692; *ibid.*, **1883**, 1716.
76. Krafft, F., *Ber.*, **16**, 3018 (1883).
76a. ——, and Noerdlinger, H., *Ber.*, **22**, 816 (1889).
77. ——, *Ber.*, **40**, 4779–4784 (1908).
78. Kreger, D. R., *Rec. trav. botan. néerland*, **41**, 603–736 (1949).—Part A.
78a. *Ibid.*, Part B.
78b. Krewson, C. F., *J. Am. Chem. Soc.*, **73**, 1365 (1951).
79. Langmuir, I., *Proc. Nat. Acad. Sci.*, **3**, 251–257 (1917).

80. Lardelli, G., and Jeger, O., *Helv. Chim. Acta*, **31**, 813–817. (1948) (in German).
81. Le Sueur, H. R., *J. Chem. Soc.*, **85**, 827 (1904); *ibid.*, **87**, 1888–1906 (1905).
82. ——, and Withers, J. C., *J. Chem. Soc.*, **107**, 736–739 (1915).
83. Levene, P. A., and Taylor, F. A., *J. Biol. Chem.*, **59**, 905–921 (1924).
84. *Ibid.*, **52**, 227–240 (1922).
85. Levene, P. A., and West, C. J., *ibid.*, **18**, 477–480 (1914).
86. ——, *et al.*, *ibid.*, **20**, 521–534 (1915).
87. ——, and Yang, P. S., *ibid.*, **102**, 541–556 (1933).
88. Lewkowitsch, J., "Chemical Technology of Oils, Fats and Waxes," 5th Ed., p. 240, London, Macmillan & Co., Ltd., 1915.
89. Lindgren, B. O., *Acta Chem. Scand.*, **I**, 779–780 (1948) (in English).
90. Lipp, A., and Kovács, E., *J. prakt. Chem.*, **99**, 243–255 (1919).
91. Lipp, A., and Casimer, E., *Ibid.*, 256–268 (1919).
92. Lycan, W. H., and Adams, R., *J. Am. Chem. Soc.*, **51**, 625–629 (1929).
93. Malkin, T., *J. Chem. Soc.*, **1931**, 2796–2805.
94. Marcusson, J., and Böttger, F., *Ber.*, **57B**, 633–635 (1924).
95. Marion, L., *Can. J. Research*, **10**, 164–169 (1934).
96. Markley, K. S., "Fatty Acids," New York, Interscience Publishers, Inc., 1947.
97. Mazee, W. M. (Batavian Petroleum Co., Amsterdam), *Rec. trav. chim.*, **67**, 197–213 (1948) (in English).
98. McKay, A. F., and Bader, A. R., *J. Org. Chem.*, **13**, 78–85 (1948).
99. Meisels, A., Jeger, C., and Ruzicka, L., *Helv. Chim. Acta*, **32**, 1075–1084 (1949) (in German).
100. Meyer, H., Brod, L., and Soyka, W. (Univ. Prag.), *Monatsh.*, **34**, 1113–1142 (1913).
101. Meyer, J. D., and Reid, E. E., *J. Am. Chem. Soc.*, **55**, 1574–1584 (1933).
102. Monick, J. A., *et al.*, *Oil & Soap*, **23**, 177–182 (1946).
103. Morgan, G. T., and Holmes, E., *J. Soc. Chem. Ind.*, **46**, 152–4T (1927); *ibid.*, **47**, 309–11T (1928).
104. Müller, Alex, *Proc. Roy. Soc.* (*London*), **A120**, 437–459 (1928).
105. Murray, K. E., and Schoenfeld, R., *J. Am. Oil Chemists' Soc.*, **28**, 461–466 (1951); *ibid.*, **29**, 416–420 (1952).
106. Nafzger, F., *Liebigs Ann. Chem.*, **1884**, 225–258.
107. Nagel, W., *Ber.*, **60B**, 605–609 (1927).
108. Nagel, W., and Mertens, W., *Ber.*, **74B**, 976–982 (1941).
109. Niemann, C., and Wagner, C. D., *J. Org. Chem.*, **7**, 227–232 (1942).
110. Normand, A. R., *et al.*, *J. Am. Chem. Soc.*, **1926**, 2362–2367.
111. O'Connor, R. T., *et al.*, *J. Am. Oil Chem. Soc.*, **28**, 154–160 (1951).
112. Penzio, G., *Gazz. chim. ind.*, **34**, II, 77 (1904).
112a. Piper, S. H., Chibnall, A. C., and Williams, E. F., *Biochem. J.*, **28**, 2175–2188 (1934).
113. Pool, W. O., and Ralston, A. W., *Ind. Eng. Chem.*, **34**, 1104–1105 (1942).
114. Prout, F. S., and Cason, J., *J. Org. Chem.*, **14**, 132–136 (1949).
115. ——, *et al.*, *J. Am. Chem. Soc.*, **70**, 298–305 (1948).
116. Pummerer, R., and Kranz, H., *Ber.*, **62B**, 2620–2628 (1929).
117. Radcliffe, L. G., and Gibson, W., *J. Soc. Dyers Colorists*, **39**, 4–10 (1923).
118. Ralston, A. W., "Fatty Acids and Their Derivatives," New York, John Wiley & Sons, Inc., 1948.
118a. Ralston, W., and Hoerr, C. W., *J. Org. Chem.*, **7**, 546–555 (1942).
118b. Rheinboldt, H., *et al.*, *Ann.*, **473**, 249–259 (1929).
119. Reindel, F., *Ann.*, **480**, 76–92 (1930).
120. Robinson, Gertrude M., and Robinson, R., *J. Chem. Soc.*, **127**, 175–180 (1925).

121. Robinson, G. M. (Mrs.), *J. Chem. Soc.*, **1934**, 1543–1545.
122. *Ibid.*, **1930**, 745–751.
123. Rothstein, B., *Bull. soc. chim.*, [5], **2**, 1936–1944 (1935).
123a. Ruben, S., *et al.*, *J. Am. Chem. Soc.*, **63**, 877–879 (1941).
124. Ruzicka, L., *et al.*, *Helv. Chim. Acta*, **20**, 1553–1556 (1937).
125. ——, *et al.*, *ibid.*, **28**, 395–399 (1945); **29**, 1611–1615 (1946).
126. ——, and Rosenkranz, G., *ibid.*, **23**, 1311–1324 (1940).
127. ——, and Wirz, W., *ibid.*, **22**, 948–951 (1939).
128. Sakurada, I., and Nakajima, A., *Chem. High Polymers*, **3**, 95–103 (1946).
128a. Sauer, J., and Adkins, H., *J. Am. Chem. Soc.*, **59**, 1–3 (1937).
129. Schaal, R., *Ber.*, **40**, 4784–4788 (1908).
129a. Schneider, A. K., and Spielman, M. A., *J. Biol. Chem.*, **142**, 345–354 (1942).
129b. Schon, L., *Soap, Perfumery & Cosmetics*, **25**, No. 1, 65–70 (1952).
130. Schuette, H. A., and Vogel, H., *Oil & Soap*, **16**, 209–212 (1939); *ibid.*, **17**, 155–157 (1940).
130a. ——, *et al.*, *J. Am. Oil Chem. Soc.*, **28**, 361–363 (1951).
131. Serwy, H., *Bull. soc. chim. Belg.*, **42**, 483–501 (1933).
131a. Siina, S., *J. Soc. Chem. Ind., Japan*, **43**, (Suppl. binding 173–174 (1940)).
132. Singleton, W. S., *et al.*, *J. Am. Oil Chem. Soc.*, **27**, 143–146 (1950).
133. Snell, F. D., and Guiteras, A. F., U.S. Patent 2,385,849 (1945).
134. Ställberg-Stenhagen, S., and Stenhagen, E., *J. Biol. Chem.*, **173**, 383–401 (1948).
134a. ——, *Arkiv. Kemi, Mineral. Geol.*, **26A**, 12 pp. (1948) (in English).
135. ——, and Stenhagen, E., *ibid.*, **18**, No. 19, 8 pp. (1945) (in English).
135a. Stenhagen, E., and Tägtström-Eketorp, B., *Arkiv. Kemi, Mineral. Geol.*, **A19**, No. 8, 10 pp. (1944) (in English).
136. Stetten, M. R., and Stetten, De Witt, Jr., *J. Biol. Chem.*, **164**, 85–91 (1946).
137. Stobbe, H., *Z. angew. Chemie*, **21**, 388 (1908).
138. Stoll, M., and Rouvé, A., *Helv. Chim. Acta*, **17**, 1283–1288 (1934).
139. ——, and ——, *ibid.*, **18**, 1087–1125 (1935).
140. Straus, F., *et al.*, *Ber.*, **66B**, 631–639 (1933).
140a. Sundwik, E. E., *Z. physiol. Chem.*, **54**, 255–257 (1907).
141. Taylor, F. A., and Levene, P. A., *J. Biol. Chem.*, **80**, 609–613 (1928).
142. Thaler, H., and Geist, G., *Biochem. Z.*, **302**, 369–383 (1939).
143. Tomecko, C. G., and Adams, R., *J. Am. Chem. Soc.*, **49**, 522–530 (1927).
144. Toyama, Y., *J. Soc. Chem. Ind., Japan*, **29**, 531–538 (1926); *ibid.*, **30**, 597–602 (1927).
144a. Tschesche, R., and Fugmann, R. (Univ. Hamburg, Ger.), *Chem. Ber.*, **84**, 810–826 (1951).
145. Tsujimoto, M., *J. Soc. Chem. Ind., Japan*, **43**, Suppl. Bdg., 22 (1939).
146. ——, *Chem. Umschau*, **30**, 33–36 (1923).
146a. Tughan, V. D., and Pink, R. C., *J. Chem. Soc.*, **1951**, 1804–1808.
147. Waentig, P., and Pescheck, G., *Z. physik. Chem.*, **93**, 529–569 (1919).
148. Wallis, E. S., and Fernholz, F., *J. Am. Chem. Soc.*, **58**, 2446–2448 (1936).
149. Whitby, G. S., *J. Chem. Soc.*, **1926**, 1458–1465.
150. Willstätter, R., and Hocheder, F., *Ann.*, **354**, 205–258 (1907).
151. Wittcoff, H., and Miller, S. E., *J. Am. Chem. Soc.*, **69**, 3138–3139 (1947).
152. Wyman, F. W., and Barkenbus, C., *Ind. Eng. Chem., Anal. Ed.*, **12**, 658–666 (1940).
153. Yamasaki, R., and Matumoto, I., *Kwagaku to Kōgyō (Science and Ind.)*, **16**, 427–429 (1941); [*Chem. Abstracts*, **36**, 288 (1942)].
154. Zhukov, A. A., and Shestakov, P. I., *J. Russ. Phys. Chem. Soc.*, **40**, 830–839 (1909).

3. The Natural Waxes

PART I: WAXES FROM INSECTS

Classification and Social Order of Wax-producing Insects

The two principal groupings of the wax-producing insects are (1) the *Apidae*, of which the honey bees are the outstanding members; and (2) the *Coccidae* to which belong the *Coccus ceriferus*, the source of Chinese insect wax, and the *Carteria lacca*, source of stick-lac.

Apidae. Under the order *Apidae* there are three genera: (1) the genus *Apis* which is of the highest social order, producing the valuable combs of wax; (2) *Melipoma*, *Trigona* and *Tetrasoma*, all rather small and stingless bees, their brood cells resembling those of the common wasp, each forming but a single layer; (3) *Bombus*, which is otherwise known as the humble or "bumble" bee, which does not swarm like the other bees.

BEESWAX

Common Honey Bee Wax

Genus Apis. This is the genus which plays the most important economic role by furnishing the beeswax of commerce. Under the genus *Apis* we find a number of species: the giant bee, *Apis dorsata*; a medium sized bee, *Apis indica*, also of Asia; *Apis florea*, the tiny East Indian bee; and lastly the domesticated honey bee, *Apis mellifica*. The honey bee was originally named *Apis mellifera* by Linnaeus in 1758, although he changed the name later to *Apis mellifica* to denote the hive-bee specifically. The term *A. mellifera* is used in a more general sense to cover honey carriers or bearers. The *Apis mellifica* produce honeycombs of almost pure wax, referred to commercially as "genuine beeswax."

There are almost as many races of *A. mellifica* and its closely allied varieties as there are countries in which bees are domesticated—that is all over the world. There are for example, the black bees of Caucasia, Carniola and Banat; the brown bees of Great Britain and Continental Europe; the yellow bees indigenous to Cyprus, northern Italy, and the Holy Land, and generally propagated in the United States; all these exist in variants or strains with mixed colors. The refined waxes obtained from these races of *A. mellifica* differ little in their physical characteristics or chemical constants.

Besides the official species, other social bees are used as honey makers and wax producers, e.g., *Apis facista* in northern Africa, which inhabits the floating apiaries of the Nile, and is regarded as the prettiest bee in the world; *Apis adansonii* in Senegal; *Apis caffra* and *Apis scutelata* in southern Africa; *Apis unicolor*, regarded as the blackest bee, a pure race domesticated in Madagascar and introduced in other parts of the world. The species in East India and the Orient produce a different kind of wax from those above mentioned; it is known as *Ghedda wax*. These East Indian species, as previously mentioned, are *Apis dorsata*, *Apis florea*, and *Apis indica* (see Ghedda Wax, p. 93).

Secretion of Wax by the Bee. The wax scales are secreted by eight wax glands on the under side of the abdomen of the worker bee. When first secreted, the wax—derived from the blood of the bee by cell action—is liquid. The secretion rapidly hardens to a pearly scale, more or less transparent, like mica. The wax scale is removed from the abdomen by a hind leg of the insect, and received by the mandible of a co-worker, where it is chewed with a secretion, before being placed in the cell of the comb. The comb is constructed in a hexagonal pattern, which provides structural strength and maximum economy of space. In the natural comb there are 4.83 cells to the linear inch, or 825 cells to the square decimeter. The bees are believed to deploy about eight pounds of honey to secrete one pound of wax.

Comb foundations are provided for hive-bees so as not to waste honey; 1½ to 3 pounds of wax can be obtained from ten combs when they are scraped. The largest amount of wax is in the foundation and in the capping, since the side walls are remarkably thin. A practice to be severely condemned is the artificial manufacture of comb foundations from hydrogenated vegetable oil wax, ceresin, paraffin, or other false waxes, as such spurious foundations eventually may find their way into the beeswax of commerce as highly undesirable impurities.

Coloration of Beeswax. Vansell and Bisson[299] of the California Agricultural Experimental Station made a study of the coloration of beeswax. Freshly secreted beeswax is white, but it readily absorbs colors from various sources. Some pollens carry yellow substances, which are liberated to the beeswax as either solid or liquid state. A cell in a new bee comb, as well as the walls of the adjacent cells, become very yellow when melted (in glass) with fresh pollens collected from various plants. It was found that color was liberated from pollen much more slowly after the grains had become dry. For example, the color imparted to white beeswax by the golden pollen of the sunflower, *Helianthus bolanderi*, is a bright orange-yellow; that of the golden pollen of the California poppy, *Papaver californicum*, a brilliant orange-yellow; that of the bright yellow dandelion, *Taraxacum*

officinale Weber, a bright yellow; that of the brown pollen of the white clover, *Trifolium repens* L., only a trace of yellow; that of the pollens of alfalfa, flax, hollyhock, and many others, none.

Much of the crude beeswax imported from Cuba and other Caribbean countries is distinctly brown. It has a strong beeswax odor, masked to some extent by a tobacco-like smell. The pollen of tobacco plants is said to be responsible for both the off-odor and the off-color of this wax. Beeswax from South American sources is often lacking in pronounced color or odor, even though free from the adulteration by paraffine, sometimes found in Chilean beeswax. Crude beeswax from West Africa has a definite yellow color and a strong beeswax odor, and is characteristically blackened at the edges of the pieces. Some of these characteristics distinguish one beeswax from another as to origin. The aromatic bodies and coloring matter in beeswax are soluble in 80 per cent ethanol and insoluble in petroleum ether.

Rendering of Crude Beeswax. Crude beeswax is usually rendered from the frames and from scrapings by melting over hot water or under solar heat. In the hot-water extraction process the container is partially filled with boiling water, and the beeswax from broken combs or cappings added. It is common practice to soak the combs in cold water for several hours before melting, so that when the wax is melted over the boiling water, it will not be absorbed by its impurities, and also to wash out the water-soluble substances. The melted wax floats on the surface, and is strained with the water through a wet cloth to remove bee and cocoon fragments and other foreign matter. Upon cooling, the wax solidifies into a cake on top of the water; dirt is removed by scraping the bottom of the cake. The straining can also be accomplished by dragging the mass with a cheesecloth fastened to a hoop, and permitting the wax to harden on cooling. The cake is then removed.

If the combs are rendered on a large scale the melted wax is removed from the hot-water container by decantation from the surface; any residue is placed in layers of straw and pressed to obtain more wax, the straw acting as a filter. A wax press employing hot water for this purpose is available; the product is called "press wax." High-or-low pressure steam is a good indirect source of heat for melting wax. The water used in the melting process should have a low mineral content. Stainless steel or aluminum is desirable for wax-processing equipment. Wood or glass makes an excellent container for the manipulation of wax, which will become contaminated by the use of iron equipment.

Solar Extraction Process. In the "solar extraction process" the crude beeswax from the cappings can be rendered by exposing it to the sun in a solar extractor. Sun melting reduces the intensity of its color and removes soluble contaminating substances by coagulation. Vansell and Bisson[299]

state that one large producer in the Sacramento Valley in California, in preparing cappings for solar extraction, lets the cuttings fall into cloth boxes, which are supported over a long, shallow draining trough, thus allowing the cappings honey to run into the general stream from the extractor. As each box is filled, it is slid along the rack and replaced by an empty one. When the cappings are sufficiently drained of honey, each box is transferred to an individual solar extractor. A long, narrow extractor could be constructed to accommodate several of these boxes, thus increasing the efficiency of the process. Galvanized iron is satisfactory construction material for the solar extractor.

In preparing the best quality of wax for commerce it is common practice to pare off the capping of the honey cells and then place the comb in a centrifugal machine (extractor), which removes the honey and leaves the comb undamaged so that it can be replaced in the hive to be refilled by the bees, and thus save the honey they would use in making a new comb. Such a prepared wax is of a good grade, as it is free from *propolis*, a greenish brown, resinous substance that the bees use in sealing the cells in the comb and for attaching it to its support. The bees obtain the resin from the branches and leaves of the birch, ash, elm, balsam, poplar and other trees. When a comb has been refilled by the bees several times and is melted down, the wax is very brown, and strong in odor.

Sources of Beeswax. More than fifty years ago Herbig attempted to show the world-wide distribution of beeswax in the following manner. Europe: Germany, Italy, Turkey, Portugal, and France. Africa: Egypt, East and West Africa. Asia: Syria, Ceylon, Singapore, Bombay, Madras, Burma. America: California, Mexico, Cuba, Haiti, Jamaica, Domingo, Brazil and Chile. It will be noted that the list is a comprehensive if not complete one. There is no other natural wax known that has so wide a distribution as beeswax (see Table 24). The United States imports much of its beeswax from Brazil, the Caribbean countries, Chile, and Benguella in West Africa (also see p. 88).

The principal source of wax in the West Coast of Africa is Benguella, a province of Angola. The extent of the exports of beeswax from these Portuguese colonies is given by Lepierre and Carvalho[153] of Lisbon:

Angola	941,372 kilograms
Mozambique	151,747
Guinea	86,836
Timor	32,655
	1,212,606

The composition of beeswax was listed by these authors as C_{27}, C_{31}, C_{29}, C_{25} acids, the corresponding alcohols, and C_{25}, C_{27}, and C_{31} hydrocarbons. However, in the light of our present knowledge it is probable that the

acids and alcohols that go to make up the esters in beeswax have an even number of carbons.

Refining Crude Beeswax. Many ways have been devised to refine beeswax and lighten its color, including a number of patented processes. A preferred method is that in which pressure is applied under water at a temperature high enough to melt the wax. A higher yield of clean wax is obtainable by the water pressure method than when using steam extractors. The addition of sulfuric acid to the water, in any amount not exceeding 5 per cent, is common practice, since it results in a lighter-colored wax with a higher yield. The use of acids other than sulfuric, or the addition of salts, is of no advantage, and is generally undesirable. The residue left after wax extraction is known as *slumgum*, and is highly colored. Hydrogen peroxide is added to the extent of about 5 per cent so that the acid water will bleach the wax (see p. 86).

If the wax has already been recovered by a steam or other extractor, it can be melted and bleached by mixing it in the molten condition with fuller's earth. This is introduced into the wax at 130°C; the temperature is then raised to 150–170°C, at which point the wax will lose color; it is then separated and filtered. The 10 per cent of blackened fuller's earth may be treated with carbon tetrachloride or other suitable solvent to effect recovery of residual wax. Animal charcoal has been effectively used in bleaching.

Bisson and Dye[30] describe a method in which the crude wax is melted in direct contact with an alkaline solution to extract the alkali-soluble impurities. The wax is then cooled and separated from the alkaline solution: it is then remelted and treated with a second aqueous solution of salt and hypochlorite. After thorough stirring, the whole is cooled and the purified wax separated.

Steam extractors are commonly used for extracting beeswax from the source of raw material. However, steam is not an effective bleaching agent. The purification of crude beeswax by steam seems to have originated in France.

Chemical and Physical Constants of Crude Beeswax. Vansell and Bisson[299] reported sixty samples of crude wax as having the following chemical and physical constants:

	Minimum	Maximum	Average	Pure
Acid value	16.8	35.8	19.2	17.0
Iodine number (Hanus)	6.8	16.4	10.2	5.8
Saponification number	89.3	149.0	96.7	84.4
Ash content (%)	0.005	0.037	0.019	near 0
Melting point (°C)	62.0	65.0	64.0	64.0±0.9
Solidifying point (°C)	60.7	63.5	62.7	63.5±0.9
Refractive index (n_D^{80})	1.4388	1.4527	1.4407	1.4402

Color: yellowish white to brown vs. white for the pure.

To this tabulation might be added the specific gravity (d^{15}) of 0.927 minimum, 0.970 maximum, and 0.953 average.

The average acid value of wax collected from the scales of the comb wax was 17, whereas that for sample of propolis from the side walls was 125. Contamination of beeswax with propolis is very objectionable in the manufacture of cosmetics and ruins the wax for candle making, but is not so objectionable when the wax is used for plant grafting, thread waxing, and waterproofing. The gums and pitches which constitute propolis are not secreted by the bees, but originate from numerous plant sources, especially species of poplar in the western states of the United States.

Minimum and maximum values for the constants of 18 samples of beeswax from hives in different parts of Uruguay were reported by Lees and Ibarra[151] as follows: sp.gr. (d^{15}) 0.9272, 0.9697; acid value 17.5, 22.4; saponification number 82.04, 105.88; ester value 63.84, 84.88; iodine number 3.36, 10.03; refractive index (n_D^{70}) 1.4424, 1.4442; impurities 0.86, 2.65 per cent.

Characteristics of Refined Beeswax. The freezing or solidifying point of yellow beeswax is about 60–61°C for waxes having a melting point of 63–64°C. The softening point (s.p.) in water for American beeswax is 49.0–53.3°C (120–128°F), which is reasonably high; and this fact makes beeswax a desirable component for wax blends that have a paraffin foundation, since it offsets the much lower softening point of the ordinary paraffins. The Fisher-Jones melting point of a specimen of pure yellow beeswax was 56° minimum, 61.5–62° bulk, and 67°C maximum.

Specimens of pure sun-bleached beeswax from a bleachery at Babylon, New York, showed a melting point of 62.2–63.3°C and saponification number 108.7 for the "semibleached"; and a melting point of 66.6°C and saponification number of 98.9 on the more expensive "fully bleached" grade. The so-called French standard for pure white beeswax calls for an appreciable higher melting point than that customarily assigned to yellow beeswax. The Fisher-Johns melting point of an old specimen of pure white beeswax was 53°C minimum, 60–61°C bulk, and 63.5°C maximum.

Cortese[60] compiled the physical and chemical constants of 24 samples of beeswax produced in various parts of Italy. The minimum and maximum values were: density (d^{15}) 0.9597–0.9680, m.p. 63–64°C, f.p. 60–61°C, refractive index (n_D^{70}) 27–30°C, (n_D^{40}) 42.9–45.9°C, acid value 19.03–20.92, saponification number 92–96.2, ester value 72.20–77.13, and iodine number 8.0–10.3. The small variations, says Cortese, indicate the uniform quality of Italian beeswax and the care exercised in its production.

Buchner recommended the use of 35 ml of $N/2$ potassium etholate for the saponification of 3.5 grams of beeswax. The time of proper saponification with potassium etholate was reported by Berg[22] as follows: German

beeswax, 2 to 3 hours, Moroccan 5, East African 6, Chinese and Tonquin up to 8.

Zöllner[332] compiled the saponification numbers by the International Commission method (6 hours) and by the Hezel method for various waxes. The values for pure beeswax were 79.7–80.6, and 91.0–91.7, respectively; and for bleached beeswax 84.2–85.3 and 91.1–93.3, respectively. In the Hezel method 3 to 5 grams of wax are heated with 40 to 50 ml of 0.5*N* KOH solution in diethylene glycol in a covered 250 ml Florence flask placed inside an oven; a little xylene can be added to facilitate solution of the wax. This method requires no blank, no reflux or water bath, only 2 hours of heating, and only one quantitative solution (0.5*N* HCl).[332]

The saponification numbers of various types of commercial beeswax have been listed by Buchner[40] as follows:

Crude	88–106
Sun-bleached	90–98
Chemically bleached	93–108
Pressed	81
Solvent-extracted	64–102
Crude Indian (Ghedda wax)	75–145

The color of beeswax is affected very adversely by contact of iron with

TABLE 20. REFRACTIVE INDEX READINGS AT DIFFERENT TEMPERATURES OF BEESWAX SAMPLES OF KNOWN PURITY[78]

Locality	At 65°C	At 75°C	At 85°C
Mexico	1.4449	1.4414	1.4380
North Carolina	1.4453	1.4416	1.4377
Wisconsin (a)	1.4460	1.4426	1.4388
(b)	1.4443	1.4406	1.4367
Cuba	1.4441	1.4403	1.4365
Habana	1.4449	1.4412	1.4375
Haiti	1.4448	1.4410	1.4374
Southern States	1.4448	1.4414	1.4374
Africa	1.4458	1.4424	1.4387
New York	1.4456	1.4420	1.4384
San Domingo	1.4488	1.4451	1.4415
Illinois	1.4460	1.4424	1.4388
Texas	1.4449	1.4413	1.4377
Iowa (a)	1.4444	1.4405	1.4368
(b)	1.4458	1.4422	1.4384
Utah	1.4450	1.4413	1.4378
California	1.4444	1.4405	1.4368
Hilo (a)	1.4436	1.4398	1.4361
(b)	1.4434	1.4398	1.4362
(c)	1.4435	1.4400	1.4375
Minnesota	1.4470	1.4433	1.4395

Note: Samples were furnished by the Bureau of Entomology to the Contracts Laboratory, Bureau of Chemistry, Washington, D. C.

wax during the rendering process, but nickel, aluminum, monel, stainless steel, and glass vessels have little or no effect. Galvanized iron is satisfactory for solar extractors, but is very objectionable for hot-water rendering. Partial clarification of the strained wax can be brought about by boiling for at least ten minutes in 5 per cent sulfuric acid. Acid treatment, followed by thorough washing, has little affect on the original acid value of the wax, but the wax appears to be slightly harder and more brittle.

The refractive indices of various beeswax samples are compared in Table 20.

The refractive index of the unsaponifiable matter of beeswax is 1.4386 at 75°C.

The hardness of beeswax varies considerably with changes in temperature and in quality. The hardness units listed below were determined by means of a Shore durometer on (1) specimen of USP beeswax (m. 61.6°C); (2) an ordinary dark yellow wax (m. 62.3°C) refined from old combs; and (3) a sun-bleached wax (m. 63.3°C) of U.S.P. quality.

	Hardness		
Temperature	of (1)	of (2)	of (3)
−7°C	—	90	—
0°C	76	87	90
10°C	65	80	88
20°C	54	73	81
25°C	47	69	76
30°C	40	—	72

Solubility of Beeswax. Beeswax is soluble in ether, chloroform, and carbon tetrachloride; partially soluble in cold benzene or carbon disulfide; sparingly soluble in cold alcohol; and partially soluble in boiling alcohol, the free acids going into solution, but the esters remaining behind. Beeswax is insoluble in water; it is soluble in vegetable oils but not in mineral oils at ordinary temperatures. With trichloroethylene, C_2HCl_3, small quantities of the free acids and the esters and most of the hydrocarbons dissolve. The soluble part melts at 54.5°C, and the insoluble part at 67.3°C.

Buchner[40] reported that ethyl ether dissolved 30 per cent of beeswax

TABLE 21. SOLUBILITY OF BEESWAX IN VARIOUS SOLVENTS
(grams of wax per 100 grams solvent)

	at 25°C	at 35°C	at 45°C
Ethanol (95% by vol.)	0.41	0.97	1.56
Benzene	24.2	64.2	106.8
V. M. & P. naphtha	5.0	20.0	41.0
Turpentine	8.0	26.0	59.0
"Solvenol"	6.0	22.0	55.0
Ethylene dichloride	1.67	4.97	20.3
Pine oil	—	5.0	27.0

at ordinary temperature, and that much of the cerotic acid, coloring matter and hydrocarbons dissolve, leaving residue richer in wax esters.

Yellow Beeswax. The name *yellow beeswax* is given to refined but not bleached beeswax of a quality which more or less conforms to the description given by the United States Pharmacopoeia (U.S.P.). The term *yellow wax* is given by artisans to any genuine refined beeswax, irrespective of its source or origin. However, the exact color, plasticity, tensile strength, ash content, etc., are important to some industries: manufacture of candles, cosmetics, dental materials, and in the arts, such as the making of wax figures. For most purposes the liberal interpretation of purity set forth by the U.S.P. suffices for its regular industrial and pharmaceutical use, and the wax is purchased under the simple designation "Beeswax, yellow, USP", instead of Domestic yellow, Puerto Rican yellow, African yellow, etc.

In pharmaceutical preparations yellow wax is either referred to as "cera flava" or simply *beeswax*, and the white wax as "cera alba," or simply *bleached beeswax*, a quality conforming to U.S.P. definition being implied. Yellow wax, according to the U.S.P.[295], is the "purified wax from the honeycomb of the bee *Apis mellifera* Linné (Fam. Apidae); and it is a solid, varying in color from yellow to grayish brown. It has an agreeable honey-like odor, and a faint, characteristic taste. It is somewhat brittle when cold, and presents a dull, granular noncrystalline fracture when broken. It becomes plastic from the heat of the hand. Its specific gravity is about 0.95".

The U.S.P. gives a melting point range between 62 and 65°C (143.6–149.0°F). The melting point is taken by the straight open capillary tube method, which is described in detail. The U.S.P. states that beeswax is insoluble in water, and sparingly soluble in cold alcohol. Boiling alcohol dissolves the cerotic acid component and a portion of the myricin. It is completely soluble in chloroform, in ether, and in fixed and volatile oils; partly soluble in cold benzene and in carbon disulfide, and completely in these liquids at 30°C.

The U.S.P. describes assay methods for determining the acid and ester values of beeswax, and gives a permissible range of 18 to 24 for the acid value, and 72 to 77 for the ester value. It also gives methods for detecting the presence of various adulterants. It states that yellow wax should be packaged and stored in well-closed containers. The yellow beeswax, U.S.P., on the market has an acid value range between 18 and 21, and an ester value range of 71 to 79. The saponification number of yellow ranges between 90 and 97. The refractive index at 65°C is 1.4434 to 1.4488. The specific gravity at 15°C is 0.960 to 0.964. The iodine number is 6 to 11.

Test Methods. Buchner recommended the use of 35 ml of $N/2$ potassium

etholate to saponify 3.5 g of wax. The time of saponification was reported by Berg as 2 to 3.5 hours for German beeswax, 5 hours for Moroccan, 6 hours for East African, and up to 8 hours for Chinese and Tonquin wax. In determining the acid value and saponification number it is better to use 2 parts of benzene and 1 part of ethanol than ethanol alone[93]. Five grams of wax are dissolved in 75 ml of the mixed solvent in determining the acid value. The saponification number is determined by boiling with 75 ml of benzene and 25 ml of *N*/KOH, dissolved in ethanol.

The German Pharmacopoeia specified the acceptable limits of the acid value of beeswax as 18.7 to 24.3; ester value 72.9 to 76.7, and ratio number (Buchner number) as 3.6 to 3.8. Buchner[39] questioned the values given in these limitations. Ryan[227], University of Dublin, claims that the specifications of a true beeswax, *Apis mellifera*, should be as follows: melting point 62–65°C, density 0.960–0.970 at 15.5°C; acid value 19–22; ester value 70–78; ratio number 3.5–3.8; iodine number about 2.12. Ryan says that adulterants, if any, may be detected by means of an uncertain melting point and high hydrocarbon content. Benguella beeswax is sometimes contaminated with *wasp wax* (saponification number 60), which causes the wax to start melting 2°C before clearing in the melting point determination, and also lowers its saponification number. Beeswax has a flash point of 242–250°C, and 245–258°C when bleached; adulterants like ceresin, japanwax, and stearic acid lower the flash point appreciably.

Bleaching of Beeswax. *Peroxide Methods.* There are several methods of bleaching that involve the use of peroxide chemicals, (a) alkaline peroxide, (b) sulfuric acid and sodium peroxide, (c) benzoyl peroxide, (d) zinc oxide with peroxides.

In the alkaline peroxide (a) process the wax is emulsified at a temperature at which the wax is molten with an alkaline solution of hydrogen peroxide (H_2O_2), having a pH which is definitely on the alkaline side. Then the emulsified wax and alkaline solution is permitted to remain in contact without agitation for a period sufficient to bleach the wax[228].

In the sulfuric acid (H_2SO_4) and sodium peroxide (Na_2O_2) process (b) [Jehlicka, G. F., U. S. Patent 1,106,221 (1914)] the beeswax is melted by direct contact with steam; the wax is drawn off after settling and treated with a solution formed of H_2SO_4 12.5, Na_2O_2 9.5, and water 978 parts, rendering the bath slightly alkaline by adding a small amount of sodium silicate solution. It is heated with steam to about 75–80°C, agitated with a current of air; the wax is drawn off into acidulated water which has been heated to boiling by injection steam, and finally the bleached wax is withdrawn.

It has been reported that the United Chemical Works at Charlottenberg, Germany, employed benzoyl peroxide (c) as a bleaching agent.

In the general procedure (d) the water is slightly acidulated with H_2SO_4 and brought to a boil. To this the crude wax is added. The impurities settle and the refined wax is removed from the top. Then more crude is added, until the impurities become excessive. In the second step the refined wax is treated with 0.5 per cent of its weight of zinc oxide and 2.5 per cent of its weight (100 vol.) of H_2O_2. The whole is agitated for four hours at 70°F. In the third step, water is added to the wax to the extent of four times the weight of the wax; the water has Na_2O_2 added to it to the extent of 5 per cent of the weight of the wax. The mixture is agitated gently and allowed to bleach overnight at 180°F. Then it is cooled somewhat and neutralized with dilute H_2SO_4 (1.5 lb of H_2SO_4 for each lb of Na_2O_2). This is decanted and washed with water-made acid with H_2SO_4 to neutralize and wash out any alkali and the zinc oxide. The method has a broad application to the bleaching of many ester waxes. Generally speaking, the time required for bleaching may be greatly shortened by conducting the bleaching operation under pressure.

Sun-bleaching. The largest user of beeswax is the cosmetic industry, which also demands the largest proportion of wax which must be white in color. White wax, or bleached beeswax, is commercially produced by exposing sheets, granules, or chips of the yellow beeswax to the sun's rays; or it may be produced by chemical bleaching. Sun-bleached beeswax seems to be preferred by most users. The bleaching is hastened if the wax is exposed to moisture and ozone of the air, as well as to light. Decolorization is hindered if the wax is covered with glass. To reduce wax to shredded or

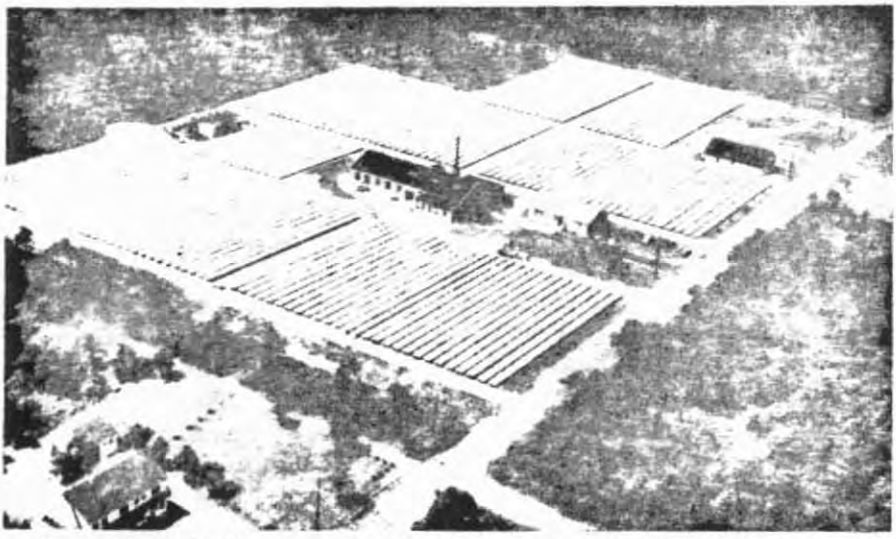


FIGURE 2. Koster Keunen sunbleached beeswax plant, Sayville, N. Y.

flake form, it is melted and while hot is poured between water-cooled rollers. The flakes are scraped from the under sides of the rollers by knives. The mass is kept wet by sprinkling with water and is frequently turned over to expose new surfaces to the sunlight. Root[234] says that to facilitate bleaching, 5 to 8 per cent of stearic acid is often mixed with the beeswax, since it tends to make it spongy so that the light penetrates deeper, and the time required for bleaching is considerably reduced. Sometimes as long as a thirty-day exposure is required to complete the bleaching process. Bisson[30a] found that a molten wax layer in pans could be bleached within 48 hours. These experiments were conducted at Wabuska, Nevada, a location favorable to sun-bleaching. The pans were of aluminum and were mounted in a trough in contact with hot water from hot springs. The molten wax layer was about 1.5 cm deep. Not all crude waxes could be so bleached, particularly those of a very dark color.

White Wax (U.S.P.). White wax, *cera alba*, as described by the United States and the British Pharmacopoeias, is bleached yellow wax. In bleaching the wax the coloring matter originating with the propolis can be destroyed by oxidation. Formerly this was always accomplished by exposing the yellow wax in thin ribbons to the effect of the sun, air, and moisture. Although this method is still practiced, at present wax is generally bleached by chemical oxidants.

White wax has a faint characteristic odor, is free from rancidity, and is nearly tasteless. It has also been described as a white shining wax, diaphanous in thin layers, inodorous, insipid, harder and less unctuous than the yellow wax. A penetrometer reading (#14 Needle, 5 sec penetration, 100 g top weight, 25°C) of a specimen of sun-bleached wax (U.S.P.) gave 11 to 11.5, contrasted to readings on two specimens of yellow beeswax of 16.5 to 17. Bleached beeswax is a trifle harder than a white microcystalline wax ("B" Square White), and about as hard as stearic acid ("Neo-Fat" 1-65). It is ductile at 35°C (95°F) and fusible at 65°C (149°F), retaining its fluidity at lower temperature. The U.S.P. specifies an ester value of not less than 72 and not more than 79, when such determinations are made in accordance with the assay methods therein described. The density of white beeswax is commonly 0.959–0.975 at 15.5°C; saponification number 85–107; acid value 17–24; ester value 65–80; Buchner ratio 3.4–3.9; hydroxyl number 15.0; iodine number (Hübl) 7–11; refractive index 1.447–1.465 at 65°C; and melting point 61–69°C.

Beeswax Imported into the United States. African beeswax, with exceptions, has somewhat different constants from the waxes of European origin, or those produced in the Americas. To some extent slight variations in the analytical constants are interlocked with the particular species of bee and its habitat, and the region producing the wax. Exceptions are

Sudan, Gold Coast, and Gambia on the west coast of Africa. Farther south on the west coast, Benguellan and Angolan waxes do not lend themselves well to bleaching methods; these waxes also have a melting point a trifle below those of United States or Canadian waxes. Waxes from the northern part of Africa, from Egypt down to Abyssinia are more or less easily bleached and are often exported in the bleached form. Abyssinia has more than one kind of wax one being reddish yellow and another a very pale yellow.

On the east coast *Kenya wax* has a density (d^{15}) of 0.949–0.965, acid value 17.3–21.6, ester value 87.1, and ratio number 3.6–4.2. *Tanyanika wax* has a somewhat higher than normal iodine value when compared with a wax on the west coast. Beeswax of Morocco and other North African regions contains a very small amount of colloidal clay, which tends to give the wax a good adhesive property. Buchner[41] gives the following constants for African beeswax: acid value 19.9, ester value 79.4, ratio number 4.0, and iodine number 11.6.

The United States is a heavy importer of beeswax from Brazil; the quality of the wax is not unlike the domestic wax. A somewhat lighter colored wax is imported from Chile. Wax of a South Brazilian wild bee (species of *Melipona* or *Trigona*) is of very inferior quality.

The beeswax of South and East Asia, also referred to as *ghedda wax*, is distinguishable from all others by a low acid value, ranging from 6.3 to 9.0, and a high ester value (85.5–99.5); the saponification number (93.2–106.1) is about the same as in other waxes[22]. The physical appearance of *Annamese beeswax* differs from that of Europea beeswax; however, when it is melted and filtered it looks like the latter. It has less free acid (acid number 7.8) and more combined acids (ester number 89.0) in the form of esters. Its Koettsdorfer value of combined acids is 9.4, and of free acids 11.0. The ester-acid ratio of the East Indian waxes is 1:9.9 to 14.9.

Hata[93] attempted to show that beeswax made by bees collecting honey from citrus trees has an entirely different composition from that of ordinary beeswax. The Formosan product contains 80 per cent of unsaponifiable substance, comprising 22.4 per cent higher alcohols, and 57.6 per cent hydrocarbons. The principal constituents are *hentriacontane* and *ceryl alcohol*, with a small amounts of *melissyl alcohol*, *nonacosane*, *heptacosane* and *pentacosane*. The fat acids of the wax consist mainly of *palmitic*, with a small amount of *oleic*, *cerotic* and *melissic acids*.

Chemical Composition of Beeswax. For over a century the chemical composition of beeswax has been a subject of investigation and discussion. The composition as given has been revised repeatedly, as a result of improved techniques used for isolation and identification of the constituents.

The first attempt to analyze beeswax for its chemical components appears to have been made in 1814. The wax was treated with boiling alcohol;

the insoluble portion (mostly esters) was separated and given the name *myricin*, and the portion which dissolved but crystallized on cooling, was designated as *cerotic acid* (m. 67°C). The soluble portion from which the cerotic acid had been removed was called *cerolein* (m. 53.5°C), and was later shown to be a complex mixture of substances. In 1845 Brodie identified myricin (m. 64.5°C as consisting principally of *myricyl palmitate* (m. 73°C). Myricin, however, is now regarded as a complex mixture of esters, only about one-third of which consists of myricyl palmitate.

According to Lewkowitsch, "normal" beeswaxes contain 13 to 17 per cent hydrocarbons, but Kebler reported 12.5 to 14.5 per cent. Hett and Ahrens[158] examined beeswaxes from various parts of the world and found that they contained 12.8 to 17.3 per cent of hydrocarbons. Many contained 15 per cent. Leys[160] estimated the hydrocarbons (m. 56°C) as 10.44 to 13.03 per cent; they had an iodine number of 13.6–15.6, indicating a melene ($C_{30}H_{60}$) content of 2.52–2.68 per cent.

The hydrocarbons of beeswax in the range of C_{15} to C_{25} are steam-distillable; the higher hydrocarbons are C_{27}, C_{29}, and C_{31}. The latter two are the chief ones, together with the unsaturated hydrocarbon, *melene*. Melene is not natural, but results from melting the wax, i.e., pyrolysis of a C_{31} monoethenoid acid constituent in the wax. Melene was thought at first to have a cyclopentene structure, but is now considered to be a straight chain. Its melting point, 62°C, was first determined by Brodie, and its constitution by Marcusson and Böttger.[174]

The amount of unsaponifiable matter consisting of alcohols plus hydrocarbons has been reported as 55.25, 52.38, 55.58, and 54.00 per cent by the following observers, respectively: Schwalb, Allen and Thomson, Lewkowitsch, and Koonce and Brown. The average unsaponifiable content is therefore 54.30 per cent, and the average hydrocarbon content is 15.05 per cent, whence the alcohols may be computed as 39.25 per cent. This agrees well with the 39.2–39.6 per cent alcohols reported by Leys for the saponified wax.

The monohydric alcohols reported by various investigators as constituents of beeswax are C_{24}, C_{26}, C_{28}, C_{30} and C_{32} alcohols as well as some with side-chain linkage, such as C_{25}, C_{27}, C_{29}, and C_{31}. There is a preponderance of C_{30}, *myricyl alcohol*, and an appreciable amount of C_{26}, *ceryl alcohol*, and C_{32}, *lacceryl alcohol* in the unsaponifiable fraction. Damoy in 1924 reported *neoceryl alcohol*, $C_{25}H_{51}OH$ (m. 77.8–78°C) as a constituent. This alcohol was described by Schwalb, and its presence was confirmed by Yamazaki and Matumoto[226] in 1941. They found that the alcohol (m. 75–76°C) could be oxidized to isopentacosanoic acid. Gascard and Damoy[88] reported the presence of a C_{27} alcohol (m. 80.2°C) and Brodie a C_{29} alcohol (m. 84°C) and a C_{31} alcohol (m. 87°C). The presence of di-, tri-, and hexahydric al-

cohols and glycerol have been indicated, but these are very minor constituents.

The mean molecular weight of beeswax in its pure state has been regarded as approximating 570. A value determined cryoscopically on an "ordinary yellow beeswax of commerce" by Findley and Brown[79] in 1953 gave 529, though the wax had a very high hydrocarbons content. These investigators also gave the concentrations in mols/kilogram for the components obtained in the molecular distillation of the commercial wax at about 0.1 micron pressure. These figures divided into 1000 give the molecular weights.

Wax Fraction	Mean Molecular Weight
150°C	340
250°C	602
Residue	885

The wax fraction (m. 59–67°C) distilling at 250°C chiefly comprises simple esters, such as myricyl palmitate and free cerotic acid. Myricyl palmitate has a molecular weight of 677.19 and cerotic acid 396.68. The residue has a very high molecular weight because of its polyester components.

In 1908 Berg[22] reported that he had isolated 0.6 per cent of *cholesterol* from both bleached and unbleached beeswax, and that this sterol wax is combined with isovaleric and lower fatty acids. The monohydric alcohols, with the possible exception of 1 per cent, are entirely in the combined state as esters of the higher fatty acids. The principal ester, *myricyl palmitate*, has the composition $C_{15}H_{31}CO \cdot O \cdot C_{30}H_{61}$, and a combining weight of 675.02.

In the light of our present knowledge, it appears that in the metamorphosis of wax by the bee a whole series of alcohols, with an even number of carbons, is initially produced by a systematic coupling of hydroxylene radicals into dimeric groupings and the coupling of such groupings.

These reactions take place with the elimination of moles of water and the linkages aided by free hydrogen. These alcohols range from C_{14} to C_{32}, but soon become oxidized by free oxygen to the corresponding C_{14} to C_{32} acid mols. However, the more immobile, or highest, alcohols combine with the lower acids of the series in preference to directly reacting with oxygen; as a result esters are formed between the C_{30} and C_{32} alcohols with the C_{14} to C_{22} acids. The chief acid of the C_{14} to C_{22} group is *palmitic*; and since the chief alcohol of the C_{30} to C_{32} group is *myricyl*, the union of these produces a large amount of *myricyl palmitate*. The C_{14} acid constituents of beeswax apparently include both *hydroxymyristic acid*, and *ω-myristlactone* (m. 33–34°C). Beeswax has a very high ester value, 72 to 76, considering the fact that it contains about 71 per cent of esters. The high ester number

is due to the presence of a large amount of hydroxy acid, in part as lactone, which requires two instead of one mole of KOH for complete saponification.

The free acids of beeswax range between 12.17 and 16.55 per cent; however, the average for yellow beeswax is 14.6 per cent. The total acids approximate 45 per cent, and the combined acids amount to about 30.4 per cent. Lewkowitsch[159] determined the molecular weights of the isolated acids from the free acids complex to be from 405.6 to 419. The free acids are in the range of C_{24} to C_{34}, the principal one of which is the C_{26} acid, *cerotic* (b) or *n*-hexacosanoic (m. 87.8°C).

The free acids present in beeswax were considered by Brodie in 1845 (Liebigs *Annal.*, **67**, 180) as having the formula $C_{27}H_{54}O_2$ (m. 78°C), which he referred to as *cerotic acid*. In 1875 Chafejeu reported the presence of a wax acid (m. 91°C) to which he assigned the formula $C_{34}H_{68}O_2$. Nafzger (Liebigs *Annal.*, 224, 225) also isolated a wax acid (m. 91°C) to which he assigned the formula $C_{30}H_{60}O_2$ or $C_{31}H_{62}O_2$, the acid known as *melissic*.

In 1923 Damoy[84, 85] determined the presence of C_{25}, C_{27}, C_{29} and C_{31} saturated wax acids in beeswax. By fractional precipitation with magnesium acetate, fractionation by molecular distillation, and recrystallization of the acids from acetone, Holde and Bleyberg[109] in 1930 found that the higher molecular weight acids of beeswax had an even number of carbon atoms, and accordingly reported the series as C_{24} to C_{32} inclusive. The propolis of the bees' comb has been reported to contain *psyllic acid*, an *iso*-acid of the formula $C_{33}H_{66}O_2$ (m. 94–95°C), with a C_{32} chain length and CH_3 side chain. The C_{25} acid (m. 77.8°C) reported by Damoy was possibly mistaken for a mixture of C_{24} and C_{26} acids. In beeswax C_{20} to C_{24} acids are not found in significant amounts, nor is C_{28} acid; C_{27} and C_{31} acids have been postulated as the chief constituents of the free "cerotic acid" component of beeswax.

Cerotic acid crystallized from the alcohol-soluble portion of beeswax, and then repeatedly recrystallized, has a Fisher-Johns melting point of 81°C maximum, 72–73°C bulk, and 61–62°C minimum.

The C_{16} acid constituents of beeswax include *palmitic*, *hydroxypalmitic* (14-hydroxyhexadecanoic), and *hypogaeic* acids. According to Toyama and Hirai (Univ. Nagoya) oxidation of the lower-melting hydroxypalmitic fraction of beeswax fat acids yields a mixture of dibasic acids consisting mainly of $HO_2C \cdot C_{12}H_{24}$, CO_2H, indicating an isomer near the 14-position of the OH group. Hypogaeic acid is the unsaturated acid otherwise known as *7-hexadecenoic acid* (m. 21°C). The C_{18} constituents of beeswax are so low in percentage that they have not been resolved.

The amount of unsaturated acids in beeswax, such as hypogaeic, was computed by Leys[160] in 1913 from the difference in the iodine number of the original wax and that of the hydrocarbons, using the factor 1.11. This computation requires a correction factor of 0.4 to be deducted from the

TABLE 22. CHEMICAL COMPOSITION OF YELLOW BEESWAX

Esters of Wax Acids: 71%
Esters (m. 64.5°C) comprise alcohols (m. 77–80°C) 60 parts and acids 42.5 parts.
Simple Esters:
$C_{15}H_{31}CO \cdot O \cdot C_{30}H_{61}$ myricyl palmitate (m. 73°C, Brodie) 23%
$C_{15}H_{31}CO \cdot O \cdot C_{32}H_{65}$ lacceryl palmitate (2%)
$C_{25}H_{51}CO \cdot O \cdot C_{30}H_{61}$ myricyl cerotate (12%)
$C_{15}H_{29}CO \cdot O \cdot C_{30}H_{61}$ myricyl hypogaeate (12%)
Hydroxy Esters:
$C_{15}H_{30}(OH) \cdot CO \cdot O \cdot C_{26}H_{53}$ ceryl hydroxypalmitate (8–9%)
Acid Esters: 4–4½% (F & B)[79]
Diesters: 6–6½ (F & B)
Acid Diesters, Triesters, Hydroxy Diesters: 3–3½% (F & B)
Cholesteryl Esters of Fatty Acids: 1%
Cholesteryl isovalerate (Berg)[23]
Coloring Matter: 1-3-dihydroxyflavone (m. 285°C) 0.3%
Lactone: ω-myristolactone (m. 33–34°C) 0.6%
Free Alcohols: C_{24}–C_{36} (?) 1–1.25%
Free Wax Acids: 13.5–14.5%
Normal acids (m. 77.5–79°C, m. wt. 412
Saturated:
Lignoceric acid (H & B)[108] 1–1½%
Cerotic acid (m. 82.5°C, Brodie) 3.8–4.4%
Montanic acid (m. 86.8°C)
Melissic acid (C_{30}, or C_{31}) (m. 90°C, Marie) 2%
Psyllic acid, $C_{32}H_{64}O_2$ (1.3–1.5%)
Unsaturated:
Hypogaeic acid, $C_{16}H_{30}O_2$ (m. 25°C, Schwalb) 1.5%
Hydrocarbons: 10.5–13.5%
Saturated:
Pentacosane, $C_{25}H_{52}$ (m. 54–54.5°C, Funcke) (0.3%)
Heptacosane, $C_{27}H_{56}$ (m. 59.5°C, Schwalb) (0.3%)
Nonacosane, $C_{29}H_{60}$ (m. 63.5°C, Damoy) (1–2%)
Hentriacontane, $C_{31}H_{64}$ (m. 68.4–69°C, Schwalb) (8–9%)
Unsaturated:
Melene, $C_{30}H_{60}$ (2.5%)
Moisture and Mineral Impurities: 1–2%

iodine number of the wax itself. Leys computed the unsaturated acids as 8.40–8.52 per cent. The unsaponifiables of beeswax have an iodine number of 4.4 based upon the original wax. A beeswax which has an iodine number of 10.2 would have (10.2 − 0.4 − 4.4) × 1.11, or 6.0 per cent of unsaturated acids.

Recovery of Acids from Beeswax. The sample of wax is extracted with boiling ethanol, and the bulk of the extractive is then distilled off. The residue is cooled and pressed to remove coloring and fatty matter. The cake of wax thus obtained is washed with boiling water, decolorized by charcoal and

filtered. It is then heated with potash lime and boiled with a large quantity of water. The solution is saturated with dilute HCl, the wax acids, in the presence of soluble calcium, being completely transformed into insoluble calcium salts, which are precipitated. These are washed, dried, and extracted by boiling alcohol and light petrolic spirit. The acids are recovered from the purified calcium salts and after the removal of a little palmitic acid, derived from the decomposition of the myricin, are found to fuse at 78–80°C[181].

Ghedda Wax

Singh reports that three species of honeybees are found in Punjab, which are suited to different climatic conditions. The Indian bee, *Apis indica* F., is found in the hilly tracts; the little bee, *Apis florea* F., in the plains where in summer the temperature may rise to 120°F or so; and the giant bee, *Apis dorsata* F., remains in the submountainous tracts and lower hills and has not been found in the higher mountains. Chinese bees are believed to be a variety of *Apis indica*, known as *Apis peroni*, and produce a very white wax.

The introduction of the artificial comb made of a paraffin composition material for use in beehives led to an acute shortage of domestic wax in Germany in 1905, and as a result foreign beeswax became a dominant factor in the German market. It became necessary then to recognize normal variations in the composition of the waxes imported from East Africa, British India, East Asia, and South America. Berg[22] found that waxes originating in South and East Asia may be distinguished from all others by a low acid number and a high ester number. Buchner had referred to the simple ratio of the ester number to the acid number as an important analytical constant, which became known as the "Buchner number," according to Berg, or simply as the "ratio number."

East Indian beeswax became later known as *Ghedda wax*, or *gedda wax*, and is defined as a wax produced by a bee other than the common honey bee, *Apis mellifica*. Buchner in 1905 conducted an extensive investigation into the species of bees that produced the beeswax imported into Germany, and found that there were a number of species of bees which he enumerated as *A. dorsata*, *A. florea*, *A. indica*, *A. fascista*, and *A. sinensis*. In his report to the *Chemiker-Zeitung* in 1906 he says that the *A. dorsata* is the largest bee, and the *A. florea* the smallest. He regarded *A. indica* or *A. fascista* as really varieties of *A. mellifica*, and stated that *A. dorsata* is a bee which builds a giant genuine two-sided comb. We now know the *A. indica* is a very distinct species, although of common size. The data on analytical constants given by Buchner are classic and instructive.

Source		M.P. (°C)	Acid No.	Sapn. No.	Iodine No.
Apis dorsata (23 samples)	mean	63.1	7.0	96.2	6.7
	max.	67.0	10.2	105.0	9.9
	min.	60.0	4.4	75.6	4.8
Apis flora (5 samples)	mean	64.2	7.5	103.2	8.0
	max.	68.0	8.9	130.5	11.4
	min.	63.0	6.1	88.5	6.6
Apis indica (7 samples)	mean	63.25	6.8	96.2	7.4
	max.	64.0	8.8	102.5	9.2
	min.	62.0	5.0	90.0	5.3
Apis mellifica	mean	63.25	20.0	95.0	7.5
	max.	65.0	21.0	99.0	11.0
	min.	61.5	17.5	87.5	4.0

The analysis of gedda wax, *A. indica* type, indigenous to various Asiatic countries has been reported as follows:

Country	Sp. Gr. 15°	M.P. (°C)	Sapn. Number	Acid Value	Ratio Number	Iodine Number
Assam (N.E. India)	0.965	61.0	97.8	5.8	16.7	5.6
Annam (Fr. Indo-China)	0.964	61.0	86.6	7.8	10.4	6.0
China	—	62.5	108.6	7.5	13.0	—
Eastern Bengal	0.973	66.4	103.2	7.6	12.2	7.7
Japan	—	65.7	94.8	6.9	13.2	12.6
Korea (*A. indica*)	—	65.6	84.5	5.8	13.4	11.4
Philippines	0.961	63.2	101.6	6.9	14.0	9.1
Macassar (Batavia)	0.956	60.5	118.8	7.0	12.0	6.6

Gedda wax is indigenous to British India, Siam, Annam, Cambodia, Tonkin, Batavia, Korea, Japan and the Philippines. The wax is generally exported from Bengal, Bombay, Madras, Burma, Shanghai, and Sind to the English market. A composite sample of wax of the secretions of *A. dorsata*, *A. florea*, and *A. indica*, with very little wax of the *Trigona* species was reported by Rangaswami (Madras) in 1941, as having a specific gravity (d_{15}^{15}) 0.963, m.p. 63.0°C, saponification number 92.0, acid value 6.1, ester value 87.9, ratio number 14.4, iodine number 5.8, and refractive index (n_D^{80}) 1.4404.

Gedda wax is pale to dark-yellow in color, quite firm in consistency, but of a fatty feel. When genuine beeswax is adulterated with gedda wax it is said to be difficult to detect the adulteration except through chemical analysis in which the constants for acid, saponification, and iodine evaluations are determined. The specific gravity of gedda wax is 0.956–0.973 at 15°C. Gedda wax melts at 60.4–66.4°C, the limits being wider than those of beeswax (63–64°C). The solidification point of gedda wax is about 60°C. The saponification number ranges from 86 to 130, acid value 3.5 to 10.5, ester value 69 to 123, and iodine number (Hübl) from 4.8 to 11.4. The ratio number (ratio of acid to ester value) limits set by Berg were 1:9.9

to 14.9 for gedda wax, contrasted with 1:2.9 to 4.5 for genuine beeswax. The moisture content has been reported as high as 5.0 per cent, insoluble in benzene 0.5 per cent, and ash 0.08 per cent, for Annamese beeswax.

Chemical Composition. The chief difference between the chemical composition of gedda wax and that of the official beeswax (so-called genuine beeswax) lies in the presence of a few per cent of fats (glycerides) in gedda wax, and the preponderance of alcohols lower than C_{30}. *Ceryl alcohol* is the chief constituent of gedda wax. Lipp and Casimer[163] found 48 per cent of ceryl alcohol, and no other. The esters of the wax contain 58.8 parts of alcohols to 44.0 parts of fatty acids, C_{14}, C_{16} and C_{18}. A small portion, not less than 4 per cent, are glycerides of these acids; the extent to which the acids are unsaturated is not known. The glycerides have the effect of giving a greasy appearance and feel to the wax that is not found in regular beeswax.

The ceryl alcohol is combined with palmitic and hydroxypalmitic acid as *ceryl palmitate* and *ceryl hydroxypalmitate*, and to a lesser extent with an isomer of the hydroxy acid. A portion of the hydroxypalmitic acid of beeswax undergoes an estolide formation, indicating that it is most likely that 16-hydroxypalmitic acid is a constituent. The melting point (m. 71–72°C) of the Lipp and Casimer isomer corresponds well to that of 7-hydroxypalmitic acid, although 14-hydroxypalmitic acid has been reported to be present in Japanese beeswax from *Apis indica*. Analytical constants of the wax have been reported as: melting point 62–63°C, acid value 6.1–5.8, ester value 91.5–90.8.

Gedda wax has an esters content higher than that of regular beeswax; it also has a higher molecular weight and melting point, but less free acids. It has a variable iodine number, possibly due to a varying amount of glycerides of unsaturated fatty acids.

The transition of pollen principles to wax by the bee seems to lie in the conversion of tripalmitin and tripalmitolein, the glycerides existing in plant principles, into monohydric alcohols, which recombine with an excess of the free acids formed. The hydrocarbons are simply the end products of metabolism, and the glycerol liberated is consumed as a food. Lipp and Casimer[163] reported the presence of traces of formol, ethanol, propanol, and resin.

As previously mentioned, in beeswax there appears to be an appreciable amount of unsaturated hydrocarbon, known as *melene*; it is apparently produced by pyrolysis when beeswax is melted. Gedda wax contains less melene than regular beeswax. Lipp and Casimer[163] isolated both *heptocosane* (5%) and *hentriacontane* (2%). These investigators reported finding 24 to 25 per cent of hydroxymargaric acid; it has now been well established that this acid was mistaken for *hydroxypalmitic*, and that the amount exceeds 20 per cent.

TABLE 23. CHEMICAL COMPOSITION OF GHEDDA WAX

Esters of Monohydric Alcohols:	78–80%
Ceryl palmitate (18–20%)	
Ceryl-16-hydroxypalmitate (57–58%)	
Ceryl-7-hydroxypalmitate (m. 72°C, L & K) 4%	
Glycerides:	4%
Saturated and unsaturated glycerides of C_{14}, C_{16} and C_{18} acids	
Sterols:	less than 1%
Cholesteryl palmitate	
Free Wax Acids:	5–6%
Cerotic acid (m. 76–77°C) 1%	
Melissic acid (L & K)	
Lacceroic acid	
Geddic acid ($C_{24}H_{48}O_2$, m. 94.5–95°C, L & K) 2%	
Hydrocarbons:	8–9%
Heptacosane (m. 59–59.5°C) 5%	
Nonacosane	
Hentriacontane (m. 68–68.5°C) 2%	
Melene ($C_{31}H_{62}$)	
Moisture and Impurities (including resin):	1½–2%

In the determinations of Lipp and Kuhn[165], of Munich, in 1913, the wax was saponified with 0.5*N* alcoholic potassium hydroxide for eight hours, neutralized with 0.5*N* hydrochloric acid, and the solution evaporated; the residue was extracted with petrolic ether. For identification the extract was dried and heated with soda lime, whence it was converted to cerotic acid, from which the following derivatives were made: methyl ester (m. 60°C), lustrous plates; acid amide, fine needles (m. 106°C, Marie 109°C); anilide, fine needles from alcohol (m. 53.5°C). The wax yielded two hydrocarbons, $C_{28}H_{54}$ and $C_{30}H_{62}$ (m. 58 and 70°C, respectively), but Lipp and Kovács[164] later showed each of the hydrocarbons to be at least one homolog higher, namely $C_{27}H_{56}$ and $C_{31}H_{64}$.

Japanese Beeswax

Japanese beeswax produced by native Japanese bees is not identical with the beeswax produced by European bees, which Ikuta[114] in 1930 reported were rapidly replacing the native bees. The differentiation of the general properties of European and Japanese beeswax depends on the species of bees. He also recognized the fact that the artificial comb has a close connection with the chemical constants of the beeswax. Pure waxes from native Japanese bees have the following characteristics: density (d_4^{100}) 0.8168–0.8232; m.p. 64.5–66.5°C, refractive index (n_{40}) 1.4557–1.4560; acid value 7.5–5.4; ester value 75.6–79.2; saponification number 83.1–84.6; iodine number (Wijs) 11.3–14.0; acetyl number 20.7–18.7; unsaponifiable constituents 58.3–56.5 per cent. The pure wax produced by

the European bee domesticated in Japan gave the following constants: density (d_4^{100}) 0.8141–0.8132; m.p. 62.0–63.5°C; refractive index (n_{40}) 1.4554; acid value 19.8–19.4; ester value 74.0–74.1; saponification number 93.8–93.5; iodine number (Wijs) 8.5–7.2; acetyl number 13.1–14.4, unsaponifiable constituents 49.5–48.6 per cent.

Japanese beeswax has been reported by Toyama and Hirai of the Nagoya Industrial Scientific Research Institute, Japan (Research Repts., No. 3, 42–45 (1951)) to have the following constants: density (d^{100}) 0.8162; melting point 61.0°C; refractive index (n_D^{70}) 1.4421; acid value 11.3; saponification number 109.5; acetyl value 11.3; iodine number 2.4; and unsaponifiable matter 55.4 per cent. It contains 15 per cent of hydroxypalmitic acid as calculated from acetyl values of four samples. Its good plasticity is attributed primarily to the presence of esters of higher alcohols (C_{24}–C_{36}) combined with hydroxylic acids [*Chem. Abstracts*, **48**, 6146 (1954)].

In 1933, Ikuta[113] reported that Japanese beeswax contained 4–6 per cent free acids (equivalent acid value 5.5–8.5), and 38–41 per cent combined acids. The wax of Toyama and Hirai more closely resembles the wax of *Apis mellifica*.

Bee Glue (Propolis)

Propolis, commonly called bee glue, is a wax-resinous substance gathered by the bee to structurally support the honeycomb and attach it to the side of the frame; to a lesser extent it serves as a varnish coating for cappings of the comb. In constructing its brood comb, the bee uses much of this so-called glue to bind leafy materials, clay, etc.

Propolis is gathered by bees from buds of poplar, birch, and similar trees which produce bud-coating gums, and is not altered by the bee before use. In its natural crude state it consists of resins, balsam, and wax, tannins, pollen, clay, etc. A comb which is cut out of a frame will yield about 4 per cent of propolis. Yellow beeswax of good quality normally contains somewhat less than 0.5 per cent of propolis. Crude dark-colored beeswax contains several per cent of the wax-soluble resins from propolis, causing the wax to become quite sticky. The resinous gums are objectionable when beeswax is used for many purposes in the arts and industries.

When crude propolis is freed from beeswax and impurities by treatment with hot water or other means, it is found to consist of several types of resin, balsam, wax, nonvolatile impurities, and volatile matter including moisture, and has an ash content of 1.9 to 2.7 per cent. The propolis resins are soluble in 96 per cent alcohol but insoluble in warm petrolic ether. Propolis balsam is soluble in petrolic ether and in 70 per cent alcohol. The nonvolatile impurities are soluble in neither alcohol nor petrolic ether.

Helfenberg[100a] stated that propolis, or bees resin, is of a greenish brown

TABLE 24. SUMMARY OF PROPERTIES OF BEESWAX

Habitat	Species	M.P. (°C)	Sp. Gr. T°C	Sapon. No.	Acid Value	Ester Value	E-A Ratio	Iodine No.	Cloud. Pt (°C)	Ref.
United States	*A. mellifica*	64.0	0.963/15	96.7	19.2	77.5	4.0	10.2	60.5	Vansell & Bisson
Cuba	*A. mellifica*	63.7	0.961	95.2	18.0	75.0	4.2	10.2	60.0	Salamon
Philippines	*A. indica*	63.2	0.961/15	101.6	6.9	95.0	14.0	9.1	59.5	Brill, *C. A.*, **10**, 3171 (1916)
Puerto Rico	*A. mellifica*									
Assam (India)	*A. florea*	63.2	0.965	103.2	7.5	95.7	12.8	5.6	56.0	Roberts & Islip, *C. A.*, **16**, 3007 (1922)
Australia	*A. mellifica*	64.2	—	95.7	19.0	76.0	4.0	9.5	—	Berg
Bengal (India)	*A. dorsata*	63.1	0.965	96.2	7.0	89.2	12.8	4.5	56.0	Roberts & Islip, *loc. cit.*
Canada	*A. mellifica*	64.2	0.964/15	89.4	18.0	71.9	4.0	10.0	60.0	Baril, *C. A.*, **28**, 6008 (1934)
Eastern Bengal	*A. indica*	64.2	0.965	96.2	6.8	89.4	13.1	7.7	56.0	Roberts & Islip, *loc. cit.*
Egypt	*A. fasciata*	63.4	—	97.1	19.4	74.0	4.0	8.0	59.8	Berg
Gold Coast	*A. mellifica*	64.5	0.829/99	90.8	20.5	70.3	3.4	—	—	Anon., *C. A.*, **5**, 220 (1911)
Ireland	*A. mellifica*	64.5	—	—	20.0	76.0	3.8	6.0	—	Ryan, *C. A.*, **8**, 2272 (1914)
No. Nigeria	*A. mellifica*	63.7	—	94.6	17.8	76.8	4.3	7.7	—	*Bull. Imp. Inst.*, **9**, 236 (1912).
Sierra Leone	*A. mellifica*	64.0	—	—	19.0	75.0	4.0	—	60.0	Salamon
South Africa	*A. adansonii*	63.5	—	—	19.1	79.4	4.1	11.6	—	Buchner, *C. A.*, **14**, 854 (1920)
Sudan	*A. mellifica*	66.0	0.821/99	84.6	20.6	64.0	3.1	6.6	—	Anon., *Bull. Imp. Inst.*, **8**, 23–31 (1910)
Eire	*A. mellifica*	63.5	—	94.0	20.0	74.0	3.7	7.0	—	Ryan, *Sci. Proc. Roy. Dublin Soc.*, **13**, 210 (1914)
Germany	*A. mellifica*	64.2	0.964	92.8	19.4	73.4	3.5	9.6	—	Berg
Greece	*A. mellifica*	64.5	0.962	93.9	18.6	75.3	4.0	8.8	—	Emmanuel
Italy	*A. mellifica*	63.5	0.964/15	94.1	19.9	74.6	3.8	9.1	60.5	Cortese, *C. A.*, **22**, 2283 (1928)
Norway	*A. mellifica*	63.0	0.962/15	95.3	16.6	78.7	4.7	6.0	—	Sebelien, *Z. angew. Chem.*, **26**, 689–92 (1914)
Poland	*A. mellifica*	63.5	—	96.8	19.3	77.2	4.0	6.7	—	Martell, *Chem. tech. Rundschau*, **44**, 1108 (1929)

Russia	*A. mellifica*	62.0	0.960	94.0	20.0	74.0	3.7	—	—	Gabrilovich, *Seifensieder Ztg.*, **36**, 1131 (1909)
Spain	*A. mellifica*	64.0	—	96.0	18.2	75.0	4.0	11.0	60.0	Salamon
Sweden	*A. mellifica*	63.5	—	96.8	20.1	76.0	3.8	9.3	—	Berg
Brazil	*A. mellifica*	65.5	0.962	96.2	19.0	77.5	4.1	9.2	—	Berg
Dominican R.	*A. mellifica*	63.5	0.962	93.5	18.5	72.0	3.9	—	60.0	Salamon
Uruguay	*A. mellifica*	64.0	0.948	95.0	19.9	74.3	3.2	6.6	—	Lees & Ibarra
Abyssinia	*A. adansonii*	63.5	0.958	94.0	19.8	74.5	3.8	—	60.0	Salamon, *J. S. Chem. Ind.*, **35**, 8–10 (1916)
East Africa	*A. scutela*	63.0	0.957	93.3	18.5	75.0	4.0	—	—	Salamon
Egypt	*A. facista*	63.4	—	97.1	19.4	74.0	4.0	8.0	59.8	Berg
Madagascar	*A. unicolor*	64.0	0.960	98.0	18.5	75.0	4.0	—	60.5	Salamon
Mozambique	*A. adansonii*	63.5	0.958	94.9	18.5	75.0	4.0	—	60.0	Salamon
Uganda (E)	*A. adansonii*	63.2	0.20/99	92.4	18.6	73.8	4.5	—	—	Anon., *Bull. Imp. Inst.*, **8**, 23–31 (1910)
Morocco (NW)	*A. mellifica*	63.5	—	95.0	19.0	76.0	4.0	—	60.0	Salamon
Smyrna	*A. mellifica*	—	—	93.0	19.0	74.0	3.9	—	64.5	Salamon
Japan	*A. indica*	65.0	0.820/100	83.8	6.5	77.4	11.9	12.7	—	Ikuta, *C. A.*, **25**, 1695, (1931)
Japan	*A. mellifica*	62.7	0.814/100	93.7	19.6	74.1	3.8	7.9	—	Ikuta
Ogaswara Is.	*A.* spp.	65.5	0.810/100	88.7	18.7	70.0	3.7	6.9	—	Ueno, *J. Chem. Soc. Japan*, **21**, 319 (1918)
Korea	*A. indica*	65.6	0.823/100	84.6	5.8	78.7	13.4	11.4	—	Ueno *Analyst*, **40**, 343 (1915)
Annam (Indo-China	*A. indica*, Var. *peroni*	61.0	0.964	94.4	7.8	86.6	10.1	6.0	—	Bellier, *Ann. chim. anal appl.*, **1906**, 366–368

color and an aromatic odor, and contains 5.96 per cent moisture and 1.91 per cent ash. In order to separate the resinous and waxy constituents, the material was extracted with chloroform and then with absolute alcohol. He found that 19.64 per cent remained insoluble in chloroform and 12.94 per cent in alcohol. The residues consisted of dirt, wood, and small insects. The wax and resin soluble in chloroform could not be separated, but that portion soluble in alcohol (6.70 %) was separated into a wax (m. 65–66°C) and a brownish resinous residue of a balsam-like nature, slightly acid, and having a saponification number of 183.89. This was found to contain a light brown aromatic substance (15.39 %) which had a saponification number of 13.32.

According to Heiduschka and Vogel[100], propolis resin melts at 67°C, but if reheated to 101°C it will not melt below 90°C. Several investigators have reported on the composition of propolis. The average resin content is about 64 per cent. Balsam, a sirupy liquid constituent, amounts to about 7 per cent, volatile matter 5½ per cent, nonvolatile impurities 6½ per cent, and resin-soluble wax 17 per cent.

Bisson, Vansell, and Dye[80a] have reported on the densities (d_{20}^{20}) of three samples of propolis as 1.033, 1.121, and 1.145. Propolis resin itself has a density (d_{20}^{20}) of 1.186. The iodine number of propolis ranges between 19.0 and 21.8, or about twice that of beeswax. Propolis resin has an iodine number between 30 and 55. The acid number of propolis is variable, but it apparently ranges from about 28 to 125. The refractive index and melting point of propolis are a trifle higher than those of beeswax. The crude waxes that are highly contaminated with propolis show higher densities, indices of refraction, acid values, and iodine numbers than does pure beeswax.

Propolis resin has an acid value of 114 to 120, and gives a red-brown color when reacted upon by a drop or two of acetic anhydride and sulfuric acid. The balsam has an acid value of 112 (minimum), and a saponification value of 173.8 (optimum). Bohrisch[21] reported the balsam as a golden yellow, clear, sirupy liquid of bitter taste and strong aromatic odor, but slightly soluble in alcohol; he gives the acid value as 74.9, and a saponification number (hot) of 165.1, and (cold) of 167.9.

Dieterich[67a] classified the resin constituents of propolis with the resinotannols of Tschirch. He was able to isolate four resins from the propolis crude resin (m. 90–106°C), namely 1½ per cent *proporesins* (m. 76–83°C), 1 per cent *α-proporesin* (m. 182–187°C), 4 per cent *β-proporesin* (m. 124–125°C), and traces of free resin acid. The balance of the crude resin consists of 70 per cent pure resin (m. 70–73°C), which when saponified yields a resin alcohol, *proporesino-tannol*, and also a propolis resin acid; 3.5 per cent of oxidation products of tannins such as phlobaphene; several per cent of volatile matter; and substances soluble in neither petrolic ether nor alcohol.

Trigona Wax

Trigona, wasp or stingless bee wax, according to Bennett and asociates[21b] is produced by a wild bee, *Meliponid* or *Trigona* species. The insects are widely spread, being plentiful in South America,[58] the Far East and particularly Tanganyika. Noted for its stickiness, the wax has been used to adulterate beeswax. The purified wax, secured by boiling with water and filtering through filter paper, had the following properties: melting point 64.6°C, specific gravity ($d_{15.5}^{15.5}$) 0.962, refractive index (n_D^{20}) 1.4625, acid value 7.9, saponification number 44.4, ester value 36.5, iodine value 98.3 (Wijs, 3 hrs.). Ullmann[288] in 1914 gave the following characteristics of what he termed *Trigonen* (Meliponen) wax: melting point 66–76°C, specific gravity (d_4^{15}) 0.961–0.963, acid value 16.2–22.8, saponification number 79.8–145.7, iodine number 30.2–49.6, unsaponifiable 55–59 per cent. This appears to be not unlike Burma black wax, a product of *Mellipona laeviceps* Dall.

Trigona wax is used to some extent in the shoe trade, but its greatest use seems to be in adulterating East Indian becswax (gedda wax) to bring up the melting point and iodine value to that of genuine beeswax; detection is difficult in the dark yellow grades of beeswax used for technical purposes. According to some reports, a considerable amount of blending of waxes is done by unscrupulous vendors in commercial centers, in which Caribbean waxes of the *Trigona* species are blended with East Indian waxes when they are available, with artificial comb material, or even with a petroleum wax. The adulterated waxes vary from pale yellow to a dark brown color. Since trigona wax is sticky, the stickiness is offset by further adulteration with paraffin. The odor is generally deficient, and occasionally the characteristic odor of beeswax can be barely detected upon melting the wax. Determination of the chemical and physical constants of the sample soon shows whether the wax is adulterated, or whether it is simply deficient in quality.

During World War II many adulterated waxes appeared on the market as pure, refined yellow beeswax. Samples taken from one shipment of a New York supplier showed the following characteristics: melting point 58.5°C, acid value 20.5–21.1, saponification number 98.0–101.9, ester value 77.0–81.4, iodine number 37.3–44.8. The wax was of a dark yellow-brown color, and of a disagreeable odor.

Another adulterated beeswax offered in the New York market contained about 30 per cent of *Trigona* wax and 70 per cent of East Indian wax. The wax was of a dirty brown color, and had the following constants: m.p. 59°C, acid value 9.7–10.0, saponification number 94.3–102.5, ester value 84.3–92.8, ratio number 1:8.45 to 9.60, iodine number 22.7–23.1.

Wax of Wild Honey Bee Comb

The composition of the cellular structure of the wild bee brood-comb differs from that of the ordinary honeycomb prepared in a beehive by the

bees for storing their excess honey. This difference has been shown by an analysis of a brood-comb obtained from a bee-tree at Millvale, Pennsylvania, compared with that of a honeycomb from the same state. The yield of wax materials, namely beeswax and propolis, from the cleaned bee brood-comb was 39 per cent, whereas the yield from the beehive honeycomb was more than 95 per cent. After freeing the living quarters of honey. brood pollen, and other waste material, including leafy matter, the cleaned cells of the comb structure, after wax and propolis extraction, yielded horny shells of sclero-albumenoid and no cellulose. The nature of the pure wax separated from both types of combs was substantially the same, but the wax extracted by solvent (chloroform) from the brood-comb showed considerably more vegetable wax constituents, which were not wholly converted to the end stage. The average cell of a brood-comb weighs 0.1126 gram, and is larger than that of a honeycomb.

Humble-Bee Wax

The bumblebee is of the order *Bombus*. There are two species, *Bombus terrestris*, which builds round nests of carded moss, and *Bombus lapidarius*, which makes its home in cavities among rocks. The quantity of wax produced by either type of bee is exceedingly small. Sundwik[256] described the wax obtained from a giant nest of *B. terrestris* as of interest because of its content of *psyllyl alcohol*—an alcohol of 32 carbons—and absence of myricyl alcohol (C_{30}), cerotic acid and palmitic acid, all of which are constituents of true beeswax, produced by the honey-bee *Apis mellifica*. Sundwik at Helsingfors also isolated an alcohol corresponding to a C_{32} or C_{34} alcohol. He named this *incarnatyl alcohol* (m. 69–70°C), but it may possibly be anteiso-tritriacontanol (C_{33}). The C_{32} isomer corresponds to *psyllostearyl alcohol* (m. 69°C).

Ullmann's German Encyclopoedia[288] refers to humble bee wax as "Hummelwachs," and gives its properties as follows: specific gravity (d^{15}) 0.960–0.969; melting point 68–72°C; acid value 18.0–19.4; saponification number 93–98.1; iodine number 5.0–7.0; and unsaponifiable 52–63 per cent.

The occurrence of wax in the lumen of the chitin hairs of *B. terrestris* has been reported by Schmidt[245]. The wax is extractable by chloroform and possesses a powerful double refraction which disappears on warming and returns on cooling. The dried hairs, however, gradually lose their double refractive power if mounted in balsam.

World Trade in Beeswax

The world trade in beeswax is extensive. The world production has been estimated at over 40 million pounds annually. In 1943 the United States produced 3,743,000 pounds, and the production in 1950 was estimated at

5,000,000 pounds. The United States imports a still larger amount, 6 to 7 million pounds, to meet its consumption demand of close to 12 million pounds per year[115a], valued at $6,300,000. The most important trading center for domestic and imported beeswax is New York City. The state of Iowa leads with a production of close to a half-million pounds, closely followed by California. Minnesota and Florida are the next largest producers. Pittsburgh is an important trading center for domestic beeswax; most of the beeswax produced in the West is shipped east, the eastern industries being the largest consumers.

About one-third of the foreign wax imported into the United States comes from Brazil, which supplies 1½ to 2 million pounds annually. Beeswax is also imported from Cuba, Chile, Portuguese colonies in Africa, Mexico, Dominican Republic, Haiti, French Equatorial Africa, etc.

In Germany, the honeycombs have in the past been made largely of ceresin. Therefore Germany has always been forced to import much of its wax, e.g., from East Africa. Russia is a very large user of beeswax and imports large amounts from Asia. Much of the India wax is exported to Great Britain and to Germany from Bengal, Bombay, Madras, Burma, and Sind. The Indian, Chinese, and Japanese insect waxes are satisfactory for many technical uses, but are barred from medical use by the Federal Food, Drug, and Cosmetic Law.

Uses of Beeswax

The uses of beeswax in the arts are numerous. Many hundreds of tons of crude beeswax have been used in the past in making candles in Russia, and this is still a thriving though dwindling industry there today. The Roman Catholic Church requires its candles to contain at least 50 per cent of beeswax, which it prefers both because of its perfumed odor when burning and because it has always regarded the bee as a sacred insect.[123] Thus it use in candles for religious purposes has always been considerable.

During World War II both the Army and Navy used several hundred tons of beeswax for adhesive tape, for sealing shells, for waterproofing and protective coatings of shells, for electrical equipment, and as a polish for airplane wings to reduce air resistance. It formed an essential ingredient in sunburn preventive creams, and in camouflage make-up creams for the armed forces. The cosmetic industry is a large user of beeswax, as a large quantity goes into facial creams.

Beeswax is used by electrotypers for taking wax impressions, and also by natural wood finishers, as it produces a well polished surface with a minimum effort of application. Root[223] records that a very satisfactory floor finish can be made by melting a pound of beeswax and stirring into it some turpentine while it is cooling, the amount depending upon whether a thick or thin paste is desired.

Beeswax is used in modelling flowers, fruits, illustrations of botanical specimens, and the finest work in the arts. In using beeswax for these purposes, a small quantity of lard oil or olive oil is added to make the wax more pliable. Lewkowitsch[157] states that modeling wax in Germany usually consists of beexwax 5, oil of turpentine 1 to 1½, and sesame oil ¼ to ½ parts. Beeswax is used extensively in the medical arts. Shoe pastes made in part with beeswax will withstand more dampness than those made with cheaper substitutes. The resistance of beeswax to extremes of heat and moisture make it of considerable value to the electrical industry for soaking windings of wire.

Pattern makers also use beeswax, as do manufacturers of carbon papers. Dentists use it to make impressions for dentures. Manufacturers of precision glassware employ beeswax in the art of etching flasks, pipettes, graduates, burettes, thermometers, etc. because of the facility with which it can be cut by a stylus, and because it resists the subsequent treatment with hydrofluoric acid, and can easily be removed from the glass after etching.

SCALE INSECT WAXES

"Scale insects" is the name given to insects belonging to the family *Coccidae* of the order *Homoptera*. They derive their name from the production by the females of a secretion which often hardens and forms a protective scale beneath which the insect lives; but some species, such as mealy bugs, are invested with a waxy secretion and a true scale is wanting. Scale insects include a number of serious plant pests; on the other hand, some species have a commercial value, notably the Chinese insect *Coccus pela*, the Japanese insects *Ceroplastes* spp., the cochineal insect *Coccus cacti*, the lac insect *Carteria lacca*, and the so-called ground pearls of the genus *Margarodes*.

Family Coccidae

There are a number of genera of the family *Coccidae* that furnish waxes, although only two have been of economic importance thus far, namely *Coccus ceriferus*, the source of the Chinese insect wax of commerce, and *Tachardia lacca*, furnishing "stick-lac" wax or, in its refined form, commercial shellac wax.

In the family *Coccidae* there is a subfamily *Coccinae*, in which the "scale" is merely the thickened surface of the insect, instead of being a separate housing of the body. The *Pulvinaria* is a genus which secretes a mass of waxy cotton-like material in which the insect places the eggs. The genus *Coccus* belongs to the *Coccinae*, as do also *Brahmea*, *Tachardia*, *Cerococcus*, and *Pulvinaria*. These insects are referred as as "coccins."

The scale insects which have a wax shell housing separated from the

body are known as "coccids." *Ceroplastes* is the best known genus; others furnishing waxes are *Iceria*, *Sasakiaspis*, *Prontapsis*, and *Tachardina*. The character of the wax changes somewhat, depending upon the species of host plant on which the insect feeds; in the Far East these plants are privet, citrus fruit, tea, etc. Most of the wax studies have been made in India, China, and Japan. The eggs deposited by the scale-insects may be transferred from one host to another to secure the best commercial yields, as in the case of *Coccus ceriferus* and the ceroplastids.

Chinese Insect Wax

Chinese insect wax, also called China wax, or "pe-la" by the Chinese, often resembles spermaceti in whiteness and crystalline appearance, but it is of greater hardness and friability. The wax is the product obtainable from the coccid insect *Coccus ceriferus* Farb., (*Coccus pela* Westwood). The U. S. Dispensatory[293] refers to the species as *Ericerus pela*. The insects are deposited on the twigs and branches of the Chinese ash, *Fraxinus chinensis* Rosburgh. The insects closely infest the twigs and become imbedded in a waxy material; when scraped off with the insects, this material constitutes the crude wax. It is purified by melting and straining. Cooper[293] in his "Travels of a Pioneer" in China tells of its production in the manner described below.

The seat of the industry is in Szechwan (province of Sze-chuen) in China. The "wax-trees" are cut down to a height of eight feet leaving no branches, the trunks sending forth shoots in the spring. The insects are cultivated in a different province (Yunnan). Here the brown pea-shaped scales containing the larvae of the wax insect are developed on an evergreen *Ligustrum luditum* Ait. (large-leaved privet) as a host. From Yunnan vast quantities of eggs or scales are shipped to Szechwan each year, where they are received in little balls the size of peas. These are suspended, enclosed in young leaves, on the shoots of the tree in March. In about two months the larvae emerging from the packets feed on the leaves. They soon attain the size of small butterflies, spreading themselves in immense number over the branches, which are so whitened by them as to seem covered with feathery snow. As it advances to the chrysalis form, the grub buries itself in a white secretion which covers all the branches an inch thick. These are then cut off near the stem and divided into small pieces, which are tied in bundles and put in large cauldrons, where they are boiled in water till the wax melts and rises to the surface. The wax is then skimmed off and run into moulds, where it hardens. It is said that 1500 insects produce 1 to 2 grams of wax; a pound of larvae scale will produce 4 or 5 pounds.

Although Chinese insect wax has been defined as a product of *Coccus ceriferus*, according to Huminski[111], there is another variety, produced by

Brahmea japonica. He states that the wax from *C. ceriferus* is a yellow wax of which *ceryl alcohol* and *cerotic acid* are the principal constituents; these occur in the form of the ester, *ceryl cerotate*. The *B. japonica* wax is a white wax which contains, in addition to ceryl alcohol and cerotic acid, an unsaponifiable cyrstalline hydrocarbon, *heptacosane*, $C_{27}H_{56}$.

Chinese insect wax is usually described as yellowish white, very hard, brittle, fibrous, crystalline, and translucent. It has a specific gravity (d_{15}^{15}) of 0.950–0.970[261], and ($d_{15}^{98.5}$) 0.809–0.811 when melted. It has no characteristic smell or taste. Chinese insect wax has an acid value of only 0.2–1.5, a saponification number of 73 to 93, an iodine number of about 1.4, and 49–50 per cent unsaponifiable matter; the refractive index is (n_D^{40}) 1.4566–1.4568.

The identification of the alcohol and acid components in Chinese insect wax has been a subject of considerable discussion. In 1920 Gascard[85] confirmed the findings of Brodie that Chinese insect wax is almost exclusively formed of the ester of *ceryl alcohol* and *cerotic acid*, to which Gascard assigned the formulas $C_{27}H_{56}O$ and $C_{27}H_{54}O_2$, respectively. Brodie claimed to have identified the same C_{27} acid (m. 78°C) in beeswax. Marie of Paris, Gauthier-Villars, in a thesis published as far back as 1895, assigned the formula $C_{25}H_{50}O_2$ (m. 77.5°C) to the cerotic acid found in beeswax. Gascard[85] prepared cerotic acid by the acetic bichromate oxidation of ceryl alcohol isolated from Chinese insect wax, and found the acid to have a melting point of 81.5–82°C, as crystallized from benzene. In 1930 Holde and Bleyberg[109] hydrolyzed the acids of Chinese insect wax, and prepared the cerotic acid by fractional "high vacuum" distillation, recrystallization from acetone, etc. The acids were identified by the Röntgen spectroscope lattice as *tetracosanoic* (*n*-lignoceric) and *hexacosanoic* (*n*-cerotic), indicating that the original C_{25} acid isolated by Marie was in reality a mixture of these C_{24} and C_{26} acids. It must be conceded, however, that the C_{27} acid of Gascard is not unlike the C_{27} acid with a methyl side chain linkage, known as *carbocerotic acid* (m. 82–82.5°C).

The highly purified wax or ester, *ceryl cerotate* (b) melts at 84°C, and may be converted to calcium cerotate; by treating the latter with glacial acetic acid, cerotic acid is obtained in a free state. Gascard, like Brodie, concluded that Chinese insect wax consists mainly of the ester of ceryl alcohol (m. 79.5–80°C) 49 per cent, combined with cerotic acid (m. 82–82.5°C) 51 per cent. Huminski[111], like Gascard[85] and Brodie, favored the formula $C_{27}H_{56}O$ for *ceryl alcohol*, which was isolated in a supposedly pure crystalline plate form. In 1897 Henriques[101] had assigned the formula $C_{25}H_{54}O$ to ceryl alcohol (m. 79–80°C). The melting point of the synthetic *n-ceryl alcohol* (hexacosanol) is 79.5–81°C.

In 1935 Collins[87] separated the *n*-carboxylic acids of Chinese insect wax

by fractional distillation of the ethyl esters under 0.5 mm vacuum. Mixtures of C_{26}, C_{28}, C_{24}, C_{30} acids were obtained. Of these esters 22 per cent of the higher fractions melted between 62.5 and 70°C (indicating montanic and myricinic acids as constituents). The presence of the C_{30} acid had not been previously reported. If the composition of Chinese insect wax were almost entirely *ceryl cerotate* (C_{26}, C_{26}) as often reported, the ester number would approach 73.2. The actual ester value of the wax is appreciably higher than this, generally above 78. Although the wax contains a little resin, this would hardly account for so high an ester value. Collins' separation of a C_{24} acid, previously isolated by Holde and Bleyberg, does account for the presence of an appreciable amount of an ester of lower molar weight and higher ester value than ceryl cerotate in the wax. The lower ester is ostensibly *ceryl lignocerate*, which has an ester value of 76.5. The lower alcohols reported as 10 per cent by Koyama he identified as *hexadecyl*, *octadecyl*, and a lower percentage of *tetradecyl alcohol*.

Yamasaki and Ogawa[327] reported on the composition of insect wax, secreted by *Ericerus pela* Charanus, as comprising *ibotaceryl alcohol*, $C_{27}H_{56}O$, *ceryl alcohol*, $C_{26}H_{54}O$, and *montanic*, *ibotacerotic* (C_{27}), *cerotic* (C_{26}), and *palmitic acids*.

The analytical constants for commercial Chinese insect wax as given by the Netherlands firm of Was de Wit N. V. are as follows: specific gravity (d_{15}^{15}) 0.932–0.970, melting point 82–84°C, acid value 0.2–0.5, and saponification number 70–80. The wax is hard and friable, and of crystalline structure. The iodine number of the pure wax is 1.4; some of the commercial

TABLE 25. CHEMICAL COMPOSITION OF COMMERCIAL CHINESE WAX

Esters of Aliphatic Monocarboxylic Acids: 93–95%
- montanyl lignocerate (m. 81°C)
- myricyl lignocerate (m. 83°C) 2%
- ceryl lignocerate (m. 79°C) 10%
- ceryl cerotate (C_{26}, C_{26}) 15%
- isoheptacosyl isoheptacosanoate (m. 82°) 60%*
- ceryl montanate (m. 85°C)
- isoheptacosyl melissate (C_{27}, C_{31})

Free Wax Acids: ½ to 1%
- cerotic acid (m. 82–82.5°C, G.)
- melissic acid

Free Monoethanoid Alcohols: less than 1%
- myricyl alcohol (m. 80°C, G.)

Resins: 1 to 1½%

Hydrocarbons: 2–3%
- heptacosane (m. 59.5°C)

* This ester which is in preponderance is the same as that referred to as *ibota*ceryl *ibota*cerotate of Koyama[160a].

waxes have a much higher iodine number. Ullmann[283] gives the saponification number as 70 to 93, and the unsaponifiable as 46 to 49 per cent.

Chinese Wax of Echigo. Koyama[140n] reported that the wax-producing insect, *Erytherus pela* Chevannel, grown on the plant, *Ligustrum ovalifolium*, yielded 87 per cent of crude wax when extracted with ether and chloroform. He identified monocarboxylic acids (presumably from the body rather than from the true wax) in the lower range as C_{14}, C_{16}, C_{18} and C_{20}. The acids found in the Chinese wax of commerce include C_{24}, C_{26}, C_{28} and C_{30}. Koyama stated that the wax consists mainly of *ceryl cerotate*, accompanied by some *melissyl cerotate*; later he reported the presence of an *ibotacerotic acid*, $C_{27}H_{54}O_2$ (m. 82°C); *cerotic acid*, $C_{26}H_{52}O_2$; and a lesser amount of an acid with the formula $C_{28}H_{56}O_2$.

Koyama[140n] reported that the total fatty acids (wax acids) of Chinese wax, collected in the province of Echigo, Japan, contained 70 per cent of the C_{27} acid, 15 per cent of the C_{26} and C_{28} acids, and 15 per cent of lower fatty acids. Oxidation of the *ceryl alcohol* and *ibotaceryl alcohol* (isoheptacosanol) of the unsaponifiable gave the corresponding C_{26} and C_{27} acids. The principal unsaponifiable substances were ibotaceryl alcohol (C_{27}) and a smaller amount of *melissyl alcohol* (C_{31} ?); the latter exists as *melissyl ibotacerotate* (C_{31}, C_{27} ester). It is most likely that a portion of the C_{27} alcohol would be combined with the C_{27} acid as the equivalent of *ibotaceryl ibotacerotate* (C_{27}, C_{27} ester).

Chinese Wax of Tsingtao. Besides the well-known Chinese wax, according to Teng-Han Tang and his associates, other insect waxes of the *Coccidae* family are found in China. These investigators collected such a sample from the neighborhood of Tsingtao. After repeated purification with chloroform, this wax was found to possess the following constants: specific gravity (d^{15}) 0.9683; melting point 50–51°C; refractive index (n^{60}) 1.4804; acid number 35–36; saponification number 146–150; iodine number (Hanus) 35–36; Reichert-Meisl number 6.5; Polenske number 4.3; unsaponifiable substance (*l*-rotatory) 26.9 per cent.

The wax was saponified with alcoholic KOH and benzene, and then refluxed with hot water. By evaporating the benzene solution, a 29.3 per cent yield of alcohol plus hydrocarbon was obtained, which product was shown to be composed of 1 part of alcohol to 3 parts of hydrocarbon. Ultimate analysis showed the alcohol (m. 78.5°C) to correspond to *ceryl alcohol* ($C_{26}H_{53}OH$) and the hydrocarbon (m. 68°C) to *hentriacontane* ($C_{31}H_{64}$). By acidifying the aqueous layer of the saponified mixture with 10 per cent HCl and extracting with ether, fat acids were obtained. An ether-insoluble substance proved to be *cholestene* ($C_{27}H_{46}$, m. 89°C). The fat acids were separated through their lead salts and gave after purification 35.7 per cent yield of saturated acid and 29.9 per cent of unsaturated acid.

The former (m. 78°C) was shown to be chiefly *cerotic acid* by analysis and molecular weight determination. Ibotacerotic acid was not isolated. They concluded that the composition of the new insect wax is *hentriacontane* 21.8, *cholestene* 4.7, *ceryl alcohol* 7.5, *cerotic acid* 35.7, and unsaturated acid 29.9 per cent.

Uses of Chinese Insect Wax. Chinese insect wax is marketed in thick round cakes weighing 16 to 20 kilograms. It is of considerable value in China and Japan, where it is used in the manufacture of candles and medicaments. Stock[261] states that it is used as a coating material for Chinese tallow candles. It is also used in treating silk and cotton fabrics to give them a sheen; in the sizing and glazing of papers; and for electrical insulation. It is seldom used in the shoe cream and polish industry, but is used to a limited extent in the manufacture of furniture polishes when it is freely obtainable as an article of commerce. The wax formulation of one American polish is said to have consisted of equal parts of carnauba wax, African beeswax, and Chinese insect wax.

Shellac Wax

This wax is derived from the lac-insect, *Carteria lacca* (*Tachardia lacca*), family *Coccidae*. The lac insect is a parasite about $\frac{1}{20}$th inch long, which feeds on the sap of the lac tree, *Croton lacciferus* L., family *Euphorbiaceae*,

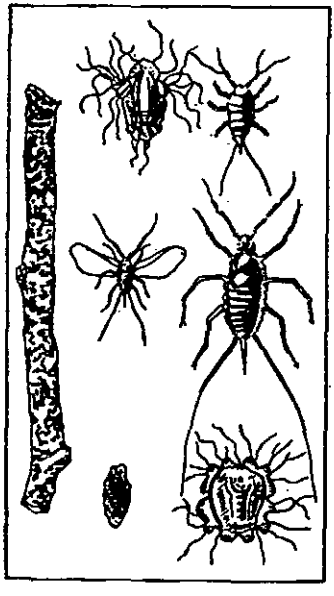


FIGURE 3. Lac bugs attached to the branch of a Lac tree. Male, female, and young insects greatly magnified.

which is indigenous to India. It is also known to suck the sap out of forty different species of host trees. These little parasites secrete the lac resin until it covers their entire body and finally merges with the exudation of its neighbor, so that one continuous coating is formed over the surface of the twig. It also secretes with the resin a red dye for which the natives find a use in dyeing silk.

Knaggs[128] states that the area in which the lac insect thrives, is about two thousand miles long by two thousand miles wide and sweeps down through India, Burma, and Thailand (Siam). Shellac is also harvested in China. In India there are four harvests a year. The Indian Lac Institute reports that for every pound of brood used for infection, the yield of shellac amounts to 3.1 to 3.7 pounds, depending on the season, type of host, and whether the infection is carried out well. Lac insects produce 10 to 48 grams per 1000 during harvest times.

The product harvested is known as "sticklac" and consists of twigs covered with incrustation about ¼ inch thick. The branches are cut or broken from the trees. The first step in producing lac resin is to spread large cloths on the ground and scrape from the branches and twigs the lac encrustations, which contain about 6 per cent of wax. After drying in the shade, the crude lac is then ground through mills to disintegrate it into a uniform product. The ground lac is then sifted clean, and the sifted lac placed in large tapered stone jars partially filled with water. Here it is stomped by the natives in order to break open the tiny lac "seeds" and free the red dye at the same time. The lac is then well washed, and spread in the sun to dry. After drying, the product is winnowed and sorted by hand for grades and sizes; the smallest size is known as *seed-lac*. Seed-lac contains 4 to 5 per cent of wax.

To produce T.N. Shellac ("truly native shell-lac"), the melted seed-lac is squeezed through a cotton bag, onto hot plates or water-cooled rollers from which it is removed in the familiar flaky form. (For a graphic detailed description of the native production of sheet shellac consult "Adventures in Man's First Plastic" by Knaggs[128].) Orange shellac prepared as described contains about 4 per cent of wax; a considerable portion of this must be removed in the course of manufacture of spirit shellac varnish, and is sold as shellac wax.

The lacs are only partially soluble in alcohol, because the wax constituent dissolves in neither ethanol nor methylated spirit at ordinary temperatures. Therefore, the wax can be made a by-product in the preparation of spirit lac. In making refined, bone dry, bleached shellac about 3 to 4 per cent of wax is obtained, based on the quantity of raw lac used.

Wax recovered at the source of origin directly from sticklac is known as *lac wax*, and the product which enters commerce has low acid and iodine values if prepared by the soda process (see Native Indian lac (shellac)

wax. A great deal of the wax which enters commerce in large amounts is the by-product obtained in the manufacture of spirit varnishes.

A resinous wax of an unidentified Venezuelan insect belonging to the *Coccidae*, and similar in physical and chemical properties to lac wax, has been reported by Müller[194a].

Native Indian Lac Wax. The pilot plant manufacture of lac (shellac) wax was undertaken by De[66] in Ranchi, Bihar, India during World War II, principally because wartime conditions hampered the importation of carnauba wax. The method of producing the shellac wax involves neither expensive equipment nor the use of alcohol. Ten pounds of sodium carbonate are dissolved in 60 gallons of water in a steam-jacketed kettle. Into this hot solution 100 pounds of seed lac is dissolved gradually, with stirring, and the hot solution (90°C) is filtered through a 100-mesh screen to remove extraneous matter. The solution is allowed to cool to 35–40°C, and 7 to 12 gallons of bleach liquor of 3 per cent "available chlorine" strength is added slowly, with stirring. After the bleach has been added the solution is heated to boiling and allowed to cool. The lac wax floats to the surface as a scum. The floating wax is scooped off and the solution filtered through a cloth and then a filter press; the shellac is precipitated by dilute sulfuric acid and further refined. The lac wax recovered in the several stages is combined, melted in water, and allowed to cool. The yield of wax is about 2.1 per cent.

In the method outlined it was found at Nankum that "Baisakhi" lac requires 12 gallons and "Kusmi" lac 7 gallons of bleach liquor, and that the respective shellac yields were 85 and 89 per cent. The shellac still contains 0.90 to 0.98 per cent of wax—an essential constituent.

Lac (shellac) wax is clean and practically odorless. It begins to soften at 72°C and melts completely at 80°C. For its general physical and chemical characteristics, see p. 112.

Dewaxing Shellac Spar Varnishes. Commercial shellac waxes are usually prepared by dewaxing shellac spirit varnishes. The London Shellac Research Bureau recommends the following procedure. Seventy-five gallons of the crude shellac varnish is mixed with 25 gallons of light petroleum spirit (d^{20} 0.7924), the mixture is heated for an half hour; then the heating is discontinued and the mixture is allowed to cool and settle. The wax particles swell and rise to the surface with the spirit, and the clear varnish can be run from the bottom of the vessel after 24 hours. The yield is 85 to 90 per cent of clear varnish. The light petroleum spirit can be used at least three times for dewaxing fresh batches of varnish. If the mixture is not heated, at least 48 hours will be required for the wax to separate. For rapid separation, concentration of lac in the varnish is critical, 3 pounds of lac per gallon of industrial methylated spirit being the optimum. For

example, 28, 36, 40, and 48 hours are required for the wax to rise to the surface when varnishes 2.5, 4.5, and 6.0 pounds "cut" per gallon, respectively, are treated with the light petroleum spirit by the heating procedure. Marwedel[181a] noted that when crude shellac is shaken with alcohol and benzin and then agitated, the mixture separates into three layers. At the top is found the wax in benzin, at the bottom shellac in alcohol, and there is an intermediate layer of undissolved, suspended wax particles.

Analytical Constants of Shellac Wax. The analytical constants of *lac wax* differ from those of by-product *shellac wax*. The latter has a higher melting point, a lower acid value, and lower saponification number. The analytical constants for lac wax of known purity were given by Singh[252a], as: acid value (A) 22.1–24.3; saponification number (B) 79.2–83.0; ester value (B–A) 57.1–60.7; iodine adsorption (Hübl after 18 hrs. action) 8.8; melting point 58–59°C. The constants for lac resin are: acid value 52–59.0, saponification number 193.5–198.4, ester value 139.1–141.4, iodine number 6.8–7.3, Endemann number 7.3–8.1. The constants are also given for various native shellacs, which vary but little from lac resin.

The Netherland firm of Was de Wit N. V. gives the analytical constants of genuine shellac wax (Schellakwas) which they offer as: specific gravity (d_{15}^{15}) 0.971–0.980, melting point 72–75°C, acid value 12–16, saponification number 120–126. F. H. Paul & Stern Brothers, New York, carry a stock of shellac wax of guaranteed purity, the constants of which are: specific gravity (d_{15}^{15}) 0.930, melting point 81–82°C, acid value 12.1 saponification number 63.8, and iodine number 6. Gillespie, Rogers, Pyatt Co., New York, has given the analytical constants of a by-product shellac wax as: melting point 82°C (close capillary), and 80°C (falling drop), direct acid value 1.2; saponification number (in butanol solution) 46.7, iodine number (Wijs) 1.25, ash 0.045 per cent, moisture and volatile 0.21 per cent.

Analytical constants appearing in the chemical literature are: specific gravity ($d^{15.5}$) 0.971–0.982, (d^{20}) 0.972, melting point 72–82°C (except native lac wax); acid value 12–24.3, saponification number 79–126, ester value 45.5–104, iodine number 6–8.8, and ash 0.08 per cent.

Shellac wax deteriorates slightly upon aging over a period of several years, as shown by the slightly reduced melting points and hardening of the wax. The physical constants determined by A. H. Warth, Jr.[312], were on specimens from the same sample before and after years of aging. (I) Melting point (drip) 83.7°C; softening point 74.5°C; ball-and-ring (m.p.) 80.7°C; Fisher-Johns (m.p.) 59°C min. and 84.5°C max.; penetrometer reading (100 g/5 sec/25°C) 6.5. (II) Melting point (drip) 82°C; softening point 74.5°C; ball-and-ring 79.8°C, Fisher-Johns 65°C min. and 82°C max.; penetrometer reading 4.25. The Fisher-Johns melting point of by-product shellac wax of another source was 77°C min., 80°C bulk, and 84°C max., as determined by McBeth[184a].

TABLE 26. COMPOSITION OF RESIN-FREE SHELLAC WAX

Esters of Wax Acids:	80–82%
Ceryl lignocerate (m. 79°C)	
Ceryl cerotate (m. 84°C)	
Lacceryl lacceroate (10–12%)	
Ceryl aleuritate (1% or less)*	
Free Wax Acids:	10–14%
Lacceroic acid (m. 95–96°C)	
Cerotic acid	
Free Wax Alcohols:	less than 1%
Neoceryl alcohol (tachardiacerol, m. 80.1°C, Tschirch)	
Lacceryl alcohol	
Hydrocarbons:	2–6%
Pentacosane (tachardiacerin) 2%	
Heptacosane	
Lac Resins:	2–4%

* Ceryl aleuritate is the ceryl ester of a trihydroxypalmitic acid known as β-aleuritic acid (m. 99–100°C).

Shellac wax has a dielectric strength varying from 356 to 416 volts per mil, which is lower than that of shellac. However, it has a breakdown voltage (BDV) which compares favorably with that of shellac, and the presence of wax in shellac facilitates proper molding in the electrical industry.

Composition of Shellac Wax. Gascard[34] examined the residual wax of stick-lac (*Tachardia lacca*) after the resin was extracted with alcohol, and isolated an ester, *lacceryl lacceroate* (m. 94°C). Upon hydrolysis the ester gave *laccerol* (lacceryl alcohol, $C_{31}H_{63}OH$), which crystallized in rhomboidal plates (m. 88°C), and *lacceroic acid* ($C_{25}H_{51}COOH$) in rhomboids (m. 95–96°C). In this way Gascard was able to prove the chemical structure of lacceryl lacceroate.

Uses of Shellac Wax. Although shellac wax is of general use in formulations where it is advantageous to use a natural wax of a hard type, its principal use is in the electrical industry. True shellac wax commands a high price, and the demand for the refined product exceeds the supply. Importations by the United States are less than 500,000 pounds per year. The high melting point of shellac wax and its high electrical insulation value favor its use in electrical potting compounds and appliances. In shoe creams the addition of a little shellac wax to an otherwise ordinary formula containing montan and paraffin waxes is a means of producing a high luster. Shellac wax sold for polishes is said to be frequently adulterated with Chinese insect wax, tallow, resin and montan wax.

Wax of *Coccus Cacti*

The cochineal insect, *Coccus cacti*, is housed in a shell of silvery appearance, the coating of which contains a wax. However, it is best known for

the red dye which it produces and which is of great value as a pigment and as a medicine. The insect feeds on the prickly pear, *Opuntia tuna* (L.) Miller. It also thrives on *Nopalea cochenillifer* L., and *Opuntia ficus indica* Mill. These thorny plants grow in the West Indies, Mexico, and elsewhere in tropical America, and are known to form wax excretions[212].

The red cochineal insect, *Pseudococcus cacti*, a native of Mexico, feeds on the cactus plant *N. cochenillifer*, commonly known as "nepal." During the rainy season, a number of the females are preserved under cover upon the branches of the plant, and after the rains have stopped they are distributed upon the plants without. They perish quickly after depositing their eggs. Hatched by the heat of the sun, these give birth to innumerable minute insects, which spread over the plant. The females, which moved about before fecundation, bury themselves in the leaves, increase rapidly in size and finally appear more like excrescences on the plant than insects. They are now gathered for use by detaching them with a blunt knife, a quill, or a feather. They are destroyed by dipping them, enclosed in a bag, into boiling water, or by the heat of a stove. If destroyed in the former manner they are subsequently dried in the sun. Cochineal is the source of *carminic acid*, which has a brilliant purple-red color.

As early as 1885 Liebermann[182] isolated the wax of the shell of the *Coccus cacti*, gave it the name of "coccerin," and assigned it the formula $C_{30}H_{60}$-$(C_{31}H_{61}O_2)_2$. Silver cochineal contains a *fat* (stearin, olein, and fatty acids); a hydroxy acid known as *cocceric acid*, $C_{31}H_{62}O_3$ (m. 92–93°C); *coccerin* 0.5–1.7 per cent; and *myristin*. The coccerin of the ordinary cochineal bug was found by Becker[31a] in 1931 to be an ester of one mol of *cocceric acid* with one mol of the dihydric *cocceryl alcohol*, and Liebermann's assumption that two mols of the acid were esterified is considered erroneous. Becker suggested the formula $C_{31}H_{62}(OH)COOH$ for the acid, and $C_{32}H_{64}(OH)_2$ for cocceryl alcohol (m. 102°C).

Chibnall and co-workers[49] found the wax to contain an unusual ketonic alcohol, namely *15-ketotetratriacontanol* (m. 100.6°C), which might have been mistaken for dihydric cocceryl alcohol. They also found that *coccerinic acid* is a mixture of *15-ketodotriacontanoic acid* (C_{32}) and *triacontanoic acid* (C_{30}); 15-keto-*n*-tetratriacontanol has the formula $CH_3(CH_2)_{13}\cdot CO\cdot (CH_2)_{13}\cdot CH_2OH$.

A coccin insect named *Coccus axin* furnishes a wax known as *axin wax*. The South African cochineal insect is known as *Dactylopius opuntiae*, or *Dactylopius coccus*.

Wax of *Pulvinaria Horii*

In 1933 Kono and Maruyama[125] reported on the wax of the coccin *Pulvinaria horii*, Kuw. He gave the following analytical constants: density

(d^{15}) 0.901; melting point 72.5–73°C; acid value 12.3; saponification number 117.1; ester value 104.7; and iodine number 6.5. The wax consists primarily of *ceryl cerotate* (m. 75–76°C), a small amount of *cerotene* ($C_{26}H_{52}$, m. 56.5°C), an unknown cyclic alcohol ($C_{22}H_{36}O$), and an unknown resin acid ($C_{14}H_{28}O_2$, $b_{1.5}$ 72–74°C).

Wax of *Cerococcus Muratae*

In 1933 Kono[134a] reported on the wax of the coccin, *Cerococcus muratae* (Kuw). It is a dark, reddish-brown resinous wax, having a high melting point (77–78°C) characteristic of the *coccin waxes* contrasted to the relatively low melting points of the *coccid waxes*. It has a density (d^{15}) of 0.906; acid value 25.2, saponification number 212.8, ester value 187.6, iodine number 15.6, acetyl value 110.4, neutral fat 72.96 per cent, unsaponifiable 15.79 per cent. The constituents isolated by Kono from a hot alcoholic extraction of the wax were *cerotic acid* (m. 78°C) and *ceryl alcohol* (m. 78°C). *Cerotic acid*, *isoceryl alcohol* (m. 62°C), and an unknown hydrocarbon (m. 47.5°C) were obtained from the portion insoluble in hot alcohol. An unidentified acid, $C_{19}H_{36}O_4$ (b_3 145°C, m. 12–12.5°C) was isolated from the portion soluble in cold alcohol.

Wax of Felted Beach Coccus

The wax from beech trees, *Fagus* spp., infected with the felted beech coccus, *Cryptococcus fagi* (Barensprung), has been reported by Blount[30c]. When crystallized from chloroform it melts at 81–81.5°C. Upon hydrolysis the acid constituent melts at 81.1–82°, and the alcohol constituent at 77.5–78°C (acetate m. 58.7–59.1°C), which can be oxidized to the same acid (ethyl ester m. 60.6°C). The acid is a ternary mixture containing 70–80 per cent of the C_{26} acid together with 30–20 per cent of the C_{24} and C_{28} acids; the alcohol consists of about 80 per cent of the C_{26} compound with 20 per cent of a mixture of the C_{24} and C_{28} compounds, the former predominating. The C_{24} alcohol is believed to be *carnaubyl alcohol*.

Coccid Waxes of Ceroplastes Family

Ceroplastes Waxes. Japanese scientists have sought to propagate certain species and strains of wax-producing insects that would furnish suitable substitutes for China wax, and yet could feed on plant life indigenous to Japan and produce with a good yield. Coccids of the order Ceroplastes have been largely employed in these investigations by entomologists and chemists. As a result, the literature on the wax-producing insects refers not only to the chemical composition of the waxes but to the composition of the bodies enclosed by the wax scale.

Perhaps the first coccid wax of the ceroplastes genera to attract atten-

tion was that of the scale-insect, *Ceroplastes rubens* (Maskell)[149]. The insect was found to inhabit two species of acacia (family Mimosaceae) which are widely distributed on the banks of the Senegal River, in French Equatorial Africa. The white insect wax of India is believed to be derived from the same species. The insect infests the twigs of a shrub or small tree, *Terminalia arjuna*, whence the name Arjun wax. A closely allied species is *Ceroplastes ceriferus* (And.). Another species which has engaged the attention of Japanese investigators is *Ceroplastes floridensis* (Comst.).

In Brazil, similar experimentation with propagation has been conducted with *Ceroplastes grandis* with *Mimosa acutifolia* as the host plant. The aim is to produce a wax superior to Arjun wax and equivalent to China wax in physical characteristics. It is to be noted, however, that all the coccid waxes have melting points appreciably lower than that of China wax or other coccin waxes.

In Australia, Hackman[95a] of the Commonwealth Scientific Industrial Research Organization at Canberra, has studied the wax extracted by means of chloroform from the insects, known as *Ceroplastes destructor*.

Composition of Ceroplastes Waxes. The studies of Kono and Maruyama[125, 127] are tabulated below so that a ready comparison may be made of several different coccid waxes, *Ceroplastes rubens*, *C. ceriferus*, and *C. floridensis*, previously referred to as Japanese insect waxes. In studying the chemical composition, Kono's method was first to separate the alcohol-soluble from the insoluble portion. The cold insoluble part, which was resin-free, was crystallized from hot alcohol, from which *melissic acid*, *ceryl alcohol*, and a *cyclic alcohol* were isolated. The chemistry of the *resin acids* and *ceresinol* was later elucidated by Kono. The differences in the Ceroplastes waxes, based on the studies of Kono[125, 127] are given below.

Arjun Wax. The wax known as Arjun wax is usually ascribed to the insect *Ceroplastes rubens*. It occurs on the twigs of trees, or host plant, in small mounds, in which form it is collected. It is not at all plentiful. The female of the coccid insect is always without wings and has either a scale-like or gall-like form; it is covered with scales of wax, which may be in the form of powder, of large tufts and plates, of a continuous layer, or a thin scale. Beneath this protecting substance lives the insect. All scale insects are plant-feeders, and obtain liquid food by means of suction. They are injurious to the plants on which they feed, but this is compensated by the economic value of the insect products obtained.

Arjun wax is moderately hard and brittle, buff in color, and of rather pleasing odor. It melts at 55 to 58°C, and has a specific gravity of 1.030 at 15/4°C, and of 0.997 at 40/40°C. Experimental investigations have been conducted in Japan to ascertain whether improved yields can be gotten by favorable change in the host plant. Koyama[140b] reported the chemical

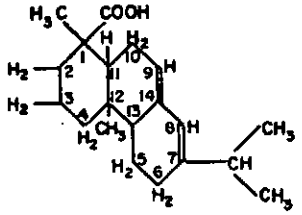
constants of the wax of *C. rubens* cultivated on tea trees to be: specific gravity (d_{40}^{40}) 0.9969, melting point 54–56°C, acid value 22.9, saponification number 152.8, and iodine number 76.3. Koyama found the yield larger, 70 per cent, when *C. rubens* was cultivated on citrus trees. This wax had the following characteristics: specific gravity (d_{40}^{40}) 0.9921, melting point 55–57°C, acid value 46.6, saponification number 126, and iodine number 130.5.

TABLE 27

	C. rubens, Mask.	*C. ceriferus*, And.	*C. floridensis*, Comst.
Density (d^{16})	1.030	0.9975	1.012
Melting point (°C)	55–58	58–58.5	49–50
Acid value	63.4	47.2	40.9
Sapon. number	139.0	139.4	97.5
Ester value	75.5	92.2	56.6
Acetyl value	23.8	57.6	80.2
Iodine number	90.3	85.3	61.6
Neutral fat (%)	36.5	19.4	27.7
Nonsaponifiable (%)	20.0	26.9	22.4
Melissic acid	isolated	detected	detected
Psyllic acid	—	detected	detected
Ceryl alcohol	isolated	detected	detected
Cyclic alcohols	$C_{11}H_{18}O$ (b_4 120°C) $[\alpha]_D^{20}$ 47.3	C_8H_{14} (b_{10} 95°C)	$C_8H_{14}O$ $C_{12}H_{22}O$ (b_2 140°C) $[\alpha]_D^{10}$ + 46.44
Melissate of cyclic alcohol	m. 68°C	detected	—
Ceryl melissate	m. 86°C	m. 85–86°C	—
Resinol	$C_{20}H_{30}O_2$ (rubenol, b_2 190°C) (opt. inactive)	$C_{16}H_{26}O$	*d*-$C_{12}H_{22}O$ (b_2 140°C) $[\alpha]_D^{10}$ + 46.44
Resin acids	(Two double bonds)		
I	$C_{20}H_{32}O_2$ (rubeabietic, m. 162–163°C) $[\alpha]_D$ − 69.2	*l*-$C_{12}H_{22}O_2$ (b_2 72–74°C) $[\alpha]_D^{20}$ − 34.77	*d*, *l*-$C_{30}H_{62}O_4$ (opt. inactive)
II	*dl*-$C_{20}H_{30}O_2$ (rubenic, m. 88°C) (opt. inactive)	*dl*-$C_{38}H_{59}O_7$ (m. 57°C)	*d*-$C_{32}H_{52}O_6$ $[\alpha]_D^{12}$ + 81.56
III	—	*dl*-$C_{28}H_{40}O_2$ (m. 43–44°C)	*d*-$C_{20}H_{30}O_2$ (m. 77°C) $[\alpha]_D^{13}$ + 16.35
IV	—	*d*-$C_{57}H_{87}O_{10}$ (m. 33–38°C) $[\alpha]_D^{20}$ + 74.62	

Koyama isolated the following constituents from the wax of *C. rubens: melissic acid, ceromelissic acid* ($C_{33}H_{66}O_2$, m. 94°C), *ceroplastic acid* ($C_{35}H_{70}O_2$, m. 96–98°C), and a resin acid, $C_{22}H_{34}O_2$. The alcohols were determined as *melissyl* and *ceroplastyl*, both primary alcohols. No ceryl or ibtoceryl(isoceryl), or their corresponding acids were found. On the other hand Kono[124] reported the presence of *n-ceryl alcohol. Ceroplastyl melissate*, the ester constituent, has the formula $C_{30}H_{61}\cdot CO\cdot OC_{35}H_{71}$ (m. wt. 957.72).

Note: The optical rotation of *rubeabietic acid* is dextro, whereas abietic acid (m. 171–173°C) derived from colophony is levo, $[\alpha]_D = 86.9°$. Abietic acid, $C_{19}H_{29}COOH$ (m. 159–161°C, $[\alpha]_D$ −77°) is a carboxylic acid of 1-methyl-7-isopropyl perhydrophenanthrene, and possesses the following structural formula:



Me group at any of positions 1, 11, 12, 13, or 14.

TABLE 28. COMPOSITION OF THE WAX OF *Ceroplastes rubens* (ARJUN WAX)

Neutral Fats: 36–37%
palmitin, stearin, olein, etc.
Alkyl Esters: 20%
ceroplastyl melissate (m. 96°C)
lacceryl cerotate (m. 89°C)
myricyl lacceroate (m. 91°C)
ceryl melissate (m. 86°C)
Free Wax Acids: 3–4%
ceroplastic (C_{34}, C_{36}), m. 96–98°C
ceromelissic (C_{32}, C_{34}), m. 94°C
melissic (C_{30}, C_{32}), m. 90°C
Resins: 34%
rubenol (resinol, b_2 190°C)
rubeabietic acid (m. 163°C)
rubenic acid (m. 88°C)
Lactones: 1–2%
4-methyl-4-decanelactone ($C_{11}H_{18}O$, $b_{4.5}$ 120–5°C)
Hydrocarbons: 3–4%
hentriacontane
cycline (cholestene)
Esters of Cyclic Alcohols (m. 68°C): less than 1%
myricyl and lacceryl esters of the cyclic alcohol, $C_{17}H_{14}O$

* The presence of so large amount of glycerides is responsible for the relatively low melting point (55–58°C) of the wax; its true wax constituents are of high melting point.

Australian Ceroplastes Wax. Hackman[95a] has studied the wax obtainable from insects, known as white wax scale, *Ceroplastes destructor*. The wax melts at 48.8°C. From the saponifiable fraction he obtained 45 per cent (original wax basis) of a substance which crystallized out from acetone in the form of colorless plates (m. 83.8°C, equivalent weight 419–420, ethyl ester m. 64°C). From the unsaponifiable there was obtained 37.5 per cent of a primary alcohol (m. 80.0°C, acetate m. 62.6°C), which upon oxidation yielded an acid (m. 83.1°C); there were no hydrocarbons. The wax has an acid value of 21.5, and an acetyl value of 37.0. He believed it to be a mixture of C_{26} and C_{28} alcohols and acids free and combined.

Brazilian Ceroplastes Wax. Mollan[102] has reported on the wax of the coccid *Ceroplastes grandis*. When the scale insects are collected from the twigs of the tree (*M. acutifolia*) in the dry season, they are found to contain 8 per cent of white wax if extracted with petrolic ether, or 10 per cent of a yellowish wax when extracted with ethyl ether. The specific gravity (d^{25}) of the purer wax is 1.002, and it melts at 49°C. The wax has a saponification number of 91.0, an acid value 30.3, and 65 per cent unsaponifiable. The yield of the wax is insufficient to make it of economic value.

Miscellaneous Coccid Waxes

Wax of *Iceria Purchasi*. Kono and Maruyama[136] in 1935 reported on the composition of the wax from the shell of the scale-insect, *Iceria purchasi* (Mask). This insect generally feeds on citrus trees as its host. A number of years ago this same species of insect threatened ruin to the orange plantations in California, where it had accidentally deposited. The blight had to be checked by parasitic insects, chiefly larvae of the ladybird beetle imported from Australia.

The properties of the wax were: specific gravity (d^{15}) 0.914, melting point 78°C, acid value 61.2, saponification number 157.5, ester value 96.3, iodine number (Hanus) 56.2, acetyl value 118.3, neutral fats 67.2 and unsaponifiable matter 31.5. From the waxy substances were isolated (in per cent) *ceryl alcohol* (9.9), *ibotaceryl alcohol* (1.7), *carnaubyl alcohol* (0.7), *cerotene* (0.3), C_{14}, C_{16} and C_{18} alcohols (0.6), *cerotic acid* (35.5), *palmitic acid* (27.3), *resin acid* $C_{10}H_{16}O_4$ (14.6), *melissic acid* (0.13) and *stearic acid* (0.8).

Wax of *Sasakiaspis Pentagona*. The scale insect, *Saskiaspis pentagona* (Tar.) is reported to yield 26.8 to 27.0 per cent of wax. The composition varies to some extent according to the species of host plant on which it feeds. The wax has a melting point of 60°C(?). *Myricyl alcohol* (27.5%), *melissic acid* (13%), *cerotic acid* (38.8%), and resinol $C_{10}H_{18}O$ (4.2%) have been given as its chemical constituents.

Wax of *Tachardina Theae*. In 1939 Kono and Maruyama[138] reported

on the coccid wax which feeds on the tea plant *Tachardina theae* (Green et Mann), found only in Formosa. From 140 parts of the wax they isolated *myricyl alcohol* 5.7, *ceryl alcohol* 6.6, *cocceric acid* 0.7, *melissic acid* 15.4, *myristic acid* 33.6, *n-hentriacontane* 0.7, *9 dodecenoic acid* 8.4, and *tetradecenoic acid* 24.4 parts. The dihydroxy acids of the latter, *dihydroxydodecanoic* and *dihydroxytetradecanoic acids*, melt at 115.2 and 127.5°C, respectively. Both glycerides of fatty acids and resin were found.

Wax of *Prontaspis Yanonensis*. Kono and Maruyama[137] in 1936 reported on a coccid wax obtained from the insect *Prontapsis yanonensis* (Kuw), the body of which consists of water, reducing sugars, cellulose, lignin, minerals, wax, pentosans, proteins, with traces of galactan and mannan. The wax content was found by these investigators to de 36.84 per cent. The wax has the following constants: density (d^{15}) 0.939, melting point 79–81°C, acid value 14.6, saponification number 86.5, ester value 72.0, iodine number 13.1, acetyl value 9.8, neutral fat 74.80 per cent, unsaponifiable 26.20 per cent. Constituents are *ceryl alcohol* 3.5, *cerotic acid* 25.0, *lauric acid* 2.0, *melissyl alcohol* 19.0, *melissic acid* 34.5, a resinol $C_{10}H_{18}O$ 8.5, and a distillate by steam distillation, 0.5 per cent.

Wax Constituents of Plant Lice

A number of ordinary parasitic insects excrete wax in minute amounts. These include psylla and aphids, of the family order *Aphididae*. From the chemical viewpoint psylla are particularly worthy of mention, since the waxes contain a very high molecular weight alcohol, acid and ester. *Psyllyl alcohol* ($C_{32}H_{66}O$) was first discovered in *Psylla alni;* and *Psylla buxi* R. also appears to contain the ester of *psyllic acid* and *psyllyl alcohol*, together with C_{30} and C_{28} compounds in lower percentages. According to Blount[30d], the wax melts at 89.6 to 90.1°C, and on hydrolysis gives an acid of 92.7°C melting point (ethyl ester, m. 68.8°C) and an alcohol which melts at 86.2°C (acetate, m. 68.7°C). The ester, *isolacceryl* (or psyllyl) *isolacceroate* (or psyllate), has a melting point of 92.5°C(?).

Waxes from Miscellaneous Insects

According to Schulz and Becker[246a] the wool louse (*Pemphigus xylostei*) which feeds on the stems of the European honeysuckle, *Lonicera xylosteum*, yields a wax (m. 108–110°C) which has "pemphygus alcohol," $C_{34}H_{68}(OH)_2$, and *pemphygic acid*, $C_{33}H_{67}OH \cdot COOH$ (m. 101–102°C) as components obtained after saponification.

The whitefly of the family order *Aleyrodidae* produces a wax before it molts. The citrus whitefly causes much injury to citrus fruit. The wax may take the form of a fringe around the sides and may more or less cover the body, and becomes quite noticeable after molting. Honeydew is produced by these insects.

The adult females of the citrus mealybug (*Pseudococcus citri* Ruso) which are pale yellow in color, are well covered by a thick waxy secretion and are ¼ inch long. The *Icerya purchasi* Mask. has a cottony-cushion scale but is not a mealy bug.

The wax moth, *Galleria mellonella* L., family Pyralididae, does not produce wax. It feeds on wax and is a pest in beehives.

The grasshopper (*Melanoplus differentialis*) produces a wax covering for its eggs. During diapause the hydropyle of the egg is water proofed by a thin layer of wax.

Wax of Cocoon Silk

The ether-soluble fraction of silk (from *Bombyx mori*) consists mainly of wax. It is unevenly distributed in the various strata of the cocoon. In yellow Italian and white Chinese cocoons the wax content, according to Bergmann[24a], decreases steadily from the external to the inside layers.

The E.S. number of silk is defined as the number of milligrams of ether-soluble material obtainable from a 10-gram sample of silk. The E.S. numbers fall between 30 and 100, and average 55. The E.S. number is indicative of the wax content of a particular silk. Removal of wax from silk by ether reduces the wetting resistance. The wax consists of a mixture of normal primary alcohols, and acids of the order C_{16} to C_{32}, paraffins of the order C_{25} to C_{31}, and liquid fatty acids. It also contains a sterol known as *bombicesterol*, associated with *cholesterol*.

PART II: WAXES FROM ANIMALS

Classification of Animal Waxes

Animal waxes are obtained from both land and marine animals. Waxes are separated from the hair-grease of the sheep, goat, llama, and dromedary[50a], although the wax of commercial importance in the land-animal group is *woolwax*. It is often called "wool fat," but erroneously so, since it contains no glycerides, of which fats are composed. "Wool grease" is the term applied to the crude soft wax obtained from the hair of the sheep, and is more specifically referred to as "degras." In wool washing, the free fatty acids and lower esters are saponified by alkali to soaps, and the unsaponified portion of the grease is commercially known as *wool fat*. In the highly refined form in which water has been blended with the wool fat, after alkali and centrifugal treatment, it is referred to as *lanolin*. If the water has been entirely removed it is called *anhydrous lanolin*.

Marine animal waxes are of two types: (a) solid marine waxes, the most important of which is *spermaceti*, and (b) liquid marine waxes. In the liquid type are sperm oil and closely allied oils, namely, any marine oil which is free, or nearly free, from glycerides (fats). Liquid marine waxes usually

contain considerable amounts of esters of unsaturated alcohols and acids, whereas the solid types contain only esters of saturated components.

WOOLWAX

Wool in the Grease. As it comes from the sheep's back, wool is called by the scourer "wool in the grease." This wool is then turned out clean with a moisture content of 16 per cent of the weight of the clean, dried wool. If washing is performed before shearing, the washed wool, freed from yolk, will consist of about 73 per cent clean wool, 13 per cent water, 5 per cent soil, 4 per cent fat, 2 per cent potassium salts or equivalent, and 2 per cent of foreign organic matter. Unwashed wools contain 45 to 62 per cent clean wool, 9 to 13 per cent water, 9 to 16 per cent soil, 10 to 24 per cent grease, 4 to 6 per cent potassium salts or equivalent, and 4 to 8 per cent foreign organic matter. In wool grease the "suint" is the saponified portion which contains the potassium salts. It is the wool fat (*woolwax*) which is recovered from the unsaponifiable that is placed on the market as *anhydrous lanolin* (*adeps lanae*), or as *lanolin* (*adeps lanae hydrosis*).

For the determination of *wool grease* in greasy wool, the sample is placed in an extraction thimble, after conditioning to a constant weight at 21.5°C and 70 per cent relative humidity, dried over sulfuric acid for at least 12 hrs at 70°C under a vacuum of 25 mm, weighed and placed in a Soxhlet extractor with petrolic ether. The extract is then freed from ether, and dried to a constant weight in a vacuum desiccator. For the determination of "suint," the degreased wool is extracted with hot water in a Soxhlet apparatus; the extract is evaporated on a water bath, dried in a vacuum desiccator, and the residue weighed.

Wool grease (yolk) and suint (water-soluble soaps) are estimated on the basis of percentages of the weights of the clean dry wool[73].

Wools	Wool grease (%)	Suint (%)
Australian	35.3–45.8	14.2–23.8
African	27.9–41.4	12.0–26.0
Peruvian	9.4–14.0	29.2–35.0
English	9.3–12.0	27.3

English merino yields 24 per cent, and Australian merino 42 per cent of woolwax on the clean dry wool basis. Lewkowitsch[157] states that the commercial yield of fully refined woolwax from New Zealand wool is 16.8 per cent, from Australian wool 16 per cent, from South American wool 13.2 per cent, and from Russian wool 6.6 per cent. South American wools are rich in yolk and require preliminary washing, while Australians do not. Washing is done with tepid water (45°C).

Wool grease of merino wool, Union of South Africa, has a refractive index of 1.4814 to 1.4681, average 1.4753 at 50°C, which is known to be best for the n readings on wool grease. If the grease is extracted from raw unwashed

wool by benzene it will have an acid number of about 93, saponification number 98.6, iodine number (Wijs) 41.8, and unsaponifiable 48.8 per cent. The same wool grease when refined to anhydrous lanolin will have an acid number of 0.2–5.6, saponification number 88 to 96, iodine number 43 to 47, and 40 to 46.6 per cent unsaponifiable.

Wool Scouring and Processes of Grease Recovery. The scouring of raw wool is done with the aid of warm soda (or potash) lye and a considerable amount of water. Scouring of wool by the soap-soda process necessitates treating it with dilute aqueous sodium carbonate at 20°C and then with an aqueous soap solution (pH of 10) at 40 to 50°C, for effective removal of the wax. The addition of 1 to 2 per cent of an organic solvent, such as benzene, to the soap solution is said to permit operating at below 40°C, thus avoiding danger of felting and attack of wool by alkali. In England the recognized type of merino wool-washing machine has been the forked-frame bowl[73]. Three to five of these machines as a unit are employed for steeping, scouring, rinsing, etc. The emulsion method of scouring is universal in England; but in North America the solvent method is largely in use, the solvent being recovered by distillation procedure for reuse. The following processes have been used to recover the grease after wool scouring.

(1) The *acid cracking process* for recovering wool grease alone.

(2) The *steeping process* for potash recovery, combined with acid treatment for grease recovery.

(3) The *battage process*, in which the effluent is kept agitated by continuous beating with hand paddles, or bats, and the grease is caused to rise to the surface in a froth, the wool grease being recovered from the foam in a yield of only 25 per cent.

(4) The *Barber jet process* is a simple combination of jets designed to give very thorough mixing for the separation of wool wax from scour liquors. Compressed air and the liquor are pumped at high velocity though a battery of the Barber jets. The particles of grease coalesce, and are thus separated from the water phase as a froth, which floats onto a trough, where it is washed with water sprays as it floats to the heating tanks. The process originated in France but has been working in England for a number of years.

(5) The *solvent process* employs benzin or other suitable solvent to extract the grease. Direct solvent extraction of wool was introduced in Europe about 1900, but the wool so treated was harsh and brittle. It was found that if the solvent extraction was so regulated that about 0.5–0.8 per cent of wax is retained by the wool, the fiber is not damaged, and can be washed to free it from suint (see p. 126).

(6) In the *flue gas treatment*, the waste liquors are treated with SO_2, or by CO_2 from purified flue gas.

(7) In the *Smith-Leach process* the scouring liquor is evaporated to a

small bulk, the grease recovered in a centrifugal machine, and the residue is incinerated for potash recovery.

(8) The *scouring liquor recovery process* removes grease from the waste liquor and the scouring liquor is used over and over again until it is rich enough in potash salts to evaporate profitably.

(9) In the *supercentrifuge process* the warm liquor is settled to remove dirt, and is then passed through a Sharples supercentrifuge to separate the grease. In the Duhamel process the wool is treated in a succession of bowls, in the first of which most of the wool-fat is removed by the scouring action of recovered suint liquor. The spent solution from this bowl is pumped to a centrifuge designed to separate sediment from the grease-laden liquor, which then passes to ordinary separators. These discharge high-grade lanolin and degreased suint. In the "Adams centrifigal process," the machine is a simple disc separator, with an extended bowl hood which has jets placed in its periphery through which the mud escapes. The effluents from the scouring plant are passed through settling tanks, usually continuously, to remove sand, and then through a screen to remove burrs and fibers; the effluent is then heated and passed to the Adams centrifuge. The feed-rate, according to Gillespie, is about 7000 gallons per hour, with a mud production of about 110 gallons per hour. A greasy emulsion is obtained, which is reheated and passed to standard centrifugal purifiers. This process originated in 1928, but in the United States it has been improved upon. Centrifugal methods are used for the recovery of approximately 90 per cent of the wool wax produced in Australia.

(10) The *frosted wool process* removes dirt from grease wools of inferior quality. It is used on a large scale in the United States. The wool is passed through a freezing chamber, and cooled to between −30 and −50°F, at which temperature the grease is congealed to a brittle solid; thus subsequent opening and dusting within the freezing chamber shakes off all the impurities, leaving a clean dry wool. About 86 to 90 per cent of the earthy, vegetable, and other foreign matters are removed from the fleece, and 33 per cent of the wax. The wool is then lightly scoured, and finally dried.

Recovery of Wool Grease by the Acid-Cracking Process. *Yorkshire Grease.* The acid cracking process is commonly employed in England for the recovery of wool grease, for example, "Yorkshire Brown Grease." The wool-scouring suds are collected in large tanks and treated with sufficient mineral acid, usually sulfuric, to "crack" the suint and scouring soaps present. The drained residue is then heated and pressed by wrapping in canvas bags to recover the crude wool grease. Yorkshire grease is distilled to obtain "spirit oil" (4%), and "distilled grease" (45.5%) which may be pressed for liquid *oleic acid*, and solid *stearine* (m. 48–53°C), "green oils" (15.5%), and pitch (14%, still residue). Water and loss are 21 per cent.

Distilled grease has 55 per cent free fatty acids, 7 per cent combined fatty acids, and 39 per cent unsaponifiable matter.

Recovered Grease. In the larger works at Bradford Corporation, compressed air and "concertina" presses are employed. The residue remaining in the press is known as "sud-cake." This by-product is rich in wool fibers, and still contains about 16 per cent of fat. The sud-cake produced in England was formerly sold in France, where it was extracted with solvent to recover the so-called wool fat, and the fat-free residue was sold as a rich fertilizer. Such grease is called "Recovered Grease" and has a more consistent composition than "Yorkshire Grease." It is obtained from the combined sewage from approximately 50 wool-scouring concerns. Such greases have various technical uses but are too impure for the preparation of lanolin.

Recovery of Woolwax by the Steeping Process. There are three steps in the ordinary practice of degreasing wool, namely (1) steeping or washing with tepid water; (2) cleansing or scouring proper with weak alkaline solutions; (3) rinsing or final washing with water. The waste from the potash scouring of wool is run into large, shallow settling cisterns, where (a) the dirt settles out in the course of 24 hours; or (b) the waste liquor or lye is passed through a centrifugal machine where dirt and grease are separated. The dirt is rich in both nitrogen and potash (K_2O). The liquor freed from dirt is siphoned into larger wooden vats which serve for the acidulation and recovery of the raw woolwax, or *straight grease.* In these vats the liquor is agitated by blasts of air from the bottom, and the sulfuric acid is sprayed evenly and gradually. When thoroughly mixed, the contents are left standing for 12 hours, and the raw wax is heated by live steam, or to a temperature of 49–52°C, so that the water can be drawn off for filtering and pressing. It is again run into settling cisterns to remove water, or it may be centrifuged to remove water from oil, depending upon which method is employed. The thoroughly cleansed product is anhydrous lanolin, an excellent emulsifying agent.

Anhydrous lanolin is comprised of about 60 per cent alcohols, and 43.5 per cent mixed fat acids (m. 41°C, iodine no. 17, m. wt. 327). The mixed alcohols have the following constants: m. p. 33°C, iodine no. 26–36, acetyl value 144, m. wt. 239.

Preparation of Hydrous Lanolin from Straight Grease. The product of the wool combers, or straight grease, if of good grade, is worked up into *hydrous lanolin.* The woolwax obtained by the steeping process above described, or by the modern supercentrifuge process, is kneaded with water for a long time, or until a water-white, colorless ointment, lanolin, is obtained. In the centrifugal recovery of woolwax, which came into extensive use in 1910, the liquors from the scouring bowls are mixed to give a content

of wax approaching 2 per cent. At a temperature of about 60°C (140°F) the liquor is settled to remove dirt, and it is then passed through a Sharples supercentriuge, which operates at a rate of about 25,000 pounds of liquor per day as a maximum. According to Ayres[15], less than 700 pounds of liquor per hour should not be allowed, as the separation is unsatisfactory at lesser speeds. The liquid wax containing about 10 per cent of water, together with water containing the dissolved detergents and soluble materials of raw wool, are discharged continuously. The water which does not contain more than 0.1 per cent of emulsified wax is acidified and again passed through the centrifuge. The waste liquor is discharged to a sewer, or treated for the recovery of potash compounds. The wax is further purified by a combination of washing and chemical bleaching agents, of which sulfur dioxide and chlorine compounds give the best results. Lanolin usually contains about 25 per cent of adsorbed moisture; the best grade is marketed as lanolin, USP.

Solvent Processes for Extraction of Woolwax. In the ordinary solvent process the greasy wool is treated with solvent naphtha in closed kiers, and the resulting solution of wool grease is transferred to stills, where the naphtha is recovered and the wool grease is obtained as a by-product. The degreased wool is next treated with a dilute tepid green-soap solution to remove the suint and dirt. The process is said to leave the fiber in much better condition, and the recovered grease may be further purified for the preparation of lanolin compounds. The finer-stapled goods usually contain the largest proportion of grease, and the amount of grease recovered is of sufficient value to retire the cost of scouring.

According to a patented process of Porter[210a], wool grease (solvent-extracted or acid-cracked grade) may be saponified with an excess of alklai, the saponified mass partially neutralized with mineral acid to a pH of 8.5 to 11, and the mixture extracted with a halogenated hydrocarbon solvent, preferably ethylene dichloride, CH_2ClCH_2Cl. Sterols and other unsaponifiables are thus recovered quantitatively.

In the older German process, described by Lach[150], for the production of lanolin, the fatty acids of the scouring liquor are removed by precipitation with magnesium hydroxide and the unsaponifiable extracted with carbon disulfide or trichloroethylene. The best solvent, according to Lach[150], is acetone. Crude lanolin, obtained by kneading the unsaponifiable with water, can be purified by bleaching it with fullers earth. Sulfur dioxide, and chlorine are said to give the best results as bleaching agents.

Hypochlorite Process for Treatment of Wool-Scouring Wastes. In the improved method of Faber and Howard[75], the objectionable organic matter of wool-scouring wastes is oxidized by calcium hypochlorite, so that a marketable clean grease with a high yield is obtained. In this process,

which was installed in a process plant, the wool-scouring waste is mixed, aerated, and then settled with calcium hypochlorite agent in an amount equal to that of the alkali used in the scour. The resulting sludge of calcium carbonate and insoluble soaps is permitted to separate by 8 hours' settling, and the clear supernatant liquid is discharged to the sewer. The sludge and scum are acidified with sulfuric acid to a pH of 4–5, producing a concentrated sludge liquor and a supernatant liquor, which is discharged. The sludge from this process is heated to 190°F and filter pressed. Steam is applied to the presses until 70 to 75 per cent of the grease is recovered. The cake may be disposed of on land and dries without odor. The grease is steamed, treated with mineral acid, and separated; it contains 2 per cent moisture and 5 to 10 per cent free fatty acid.

Hypochlorite Bleaching of Wool Grease. Woodward and Malstrom[823] have bleached wool grease satisfactorily with a mixture of sodium hypochlorite (NaOCl) and sodium chlorite ($NaClO_2$). For example, 4000 lbs of crude wool grease is heated in a lead-lined open-top kettle; 430 lbs of NaOCl solution (12 per cent available Cl) are added and mixed in. The pH of the aqeous layer is now 10.2. Immediately there are added 40 lb of $NaClO_2$ (130 per cent available Cl) dissolved in 400 lb of water. The pH is now 10.1. The mixture is heated to 170°F and stirred 1½ hr, at which time the pH is 9.6. The wool grease is water-washed to remove salts, and dried. The color is greatly enhanced and it is stable over a long period.

Physical and Chemical Characteristics of Woolwax. The United States Pharmacopoeia[295] defines *lanolin*, or "hydrous wool fat," as wool fat containing not less than 25 per cent and not more than 30 per cent water. *Anhydrous lanolin*, "wool fat," or woolwax, is a brownish yellow, tenacious, unctuous mass, having not more than a slight odor when pure. It is insoluble in water, but mixes without separation with about twice its weight of water. It is sparingly soluble in cold alcohol, more soluble in hot alcohol, and freely soluble in ether and chloroform. Refined anhydrous lanolin is fully described by the United States Pharmacopoeia[295] as to limitations of impurities when used as a medicament, namely *adeps lanae*. It defines *anhydrous lanolin* as the purified, anhydrous, fat-like substance from the wool of sheep, *Ovis aries* Linné. (Fam. Bovidae). The British Pharmacopoeia[37] defines wool fat as "the purified chlosterin-fat of sheep's wool." U.S.P. specifies a melting range of between 36 and 42°C. Benedikt[296], one of the early investigators, gave the melting point of woolwax (German) as 36 to 41°C. The solidifying point is considerably lower, or about 30°C. The index of refraction is 1.4781 to 1.4822, and 1.465 at 60°C for Yorkshire grease. Woolwax rotates the plane of polarized light to the right: $[\alpha]_D^{35}$ 6.70 (Walden).

The chemical constants vary according to the origin of the raw stock and

the nature of the process employed in refining. U.S.P. states that when the "wool fat" is dried to constant weight on a water bath with frequent stirring it should lose not more than 0.5 per cent of its weight; it should contain not more than 350 parts per million of chloride; and it should not leave more than 0.1 per cent of residue on ignition. Woolwax should be free from traces of alkali, and contain no water-soluble oxidizable impurities. If 500 mg of woolwax is boiled with 40 ml of dehydrated alcohol, the solution should be clear, or not more than opalescent if the sample is free from petrolatum.

The U.S.P. states that the free acids in 10 grams of "wool fat" require for neutralization not more than 2 cc of 0.1*N* sodium hydroxide. This is equivalent to limiting the acid value to 1.12 maximum. Ordinary grades of anhydrous lanolin have an acid value of 5.6 to 12.0. Cosmetic grades have a lower acid value than U.S.P. grades. The saponification number ranges between 82 and 127, and the ester value (excluding estolidic esters) from 73 to 77. The U.S.P. specifies an iodine number of 18 to 36 (Hanus). Ordinary grades of anhydrous lanolin have an iodine number (Wijs) of 15 to 56, Reichert-Meisl number 4.7 to 6.9, hydroxyl value 23 to 53, unsaponifiable 32 to 52 per cent, glycerol content 0. The mixed fatty acids (52 to 63 per cent) melt at about 41.8°C, and have a hydroxyl value 102–168, an iodine number about 17, and a molecular weight 364 to 393. Wool fat alcohols have acetyl and hydroxyl numbers of 160 and 181.8 respectively (average molecular weight on fatty alcohol basis 324, equivalent to $C_{22}H_{46}O$, if computed on a fatty alcohol basis). The diestolidic esters, which occur in woolwax in amounts up to 31 per cent, according to Bertram, have a molecular weight of about ±800. De Navarre has given criterion figures on samples of lanolin from nine different American suppliers: acid value 0–0.56, saponification number 90–100, iodine number (Hanus) 18 to 32, specific gravity (d^{25}) 0.924 to 0.965, ash 0–0.1 per cent, free cholesterol 1.14–8.0 per cent, combined cholesterol 8–15.3 per cent, total cholesterol 12 to 24 per cent. *Lanolin concentrates:* acid value 0.83–1.0 per cent, saponification number 5.5–25, iodine number (Hanus) 28–35, sp. gr. (d^{25}) 0.980, m.p. 54.4–60°C, ash 0 to 0.19 per cent, moisture 0–0.19 per cent.

Woolwax is difficult to saponify, and in making an assay the saponification number will increase appreciably as the time of saponification is lengthened. According to Utz[256], on a sample of German woolwax the saponification number increased in steps from 84.2 for ½ hour to 151.6 for 9 hours. This is attributed to the esters with (a) high molar alcohols, (b) triterpene alcohols, and (c) sterols, combined with more or less high molar acids. Heiduschka and Nier[99a] obtained 32.8 per cent of unsaponifiable matter, consisting of the above constituents. The unsaponifiable, when distilled at 3 mm Hg, at 270–310°C yields terpenes and lower alcohols as

TABLE 29. PHYSICAL AND CHEMICAL CONSTANTS FOR ANHYDROUS TECHNICAL LANOLIN

Kind	Sp. Gr. @ 15/15°C	M.P. (°C)	Acid Value	Sapon. No.	Iodine No.	Unsapon. Matter (%)
Australian	0.940	—	5.9–15.5	102.4–113.3	16.5–29.5	45–51.4
German	0.932–0.944[141]	37.5–40.0	12.3–22.0	84.2– 98.3	15.3–17.8	35–45
Hungarian	—	—	5.6 max	88.1– 95.6	42.7–46.9	40–46.4
New Zealand	—	—	14.3	110.5–112.5	26.5	44
North American	0.932–0.945	38.0–40.0	11.9	82.0–127.0	15.0–36.0	39–44
Russian	—	—	13.9	94.2– 95.0	—	39
Yorkshire	$0.943_{17°}$	36.0–43.0	—	80.0–100.0	20.0–29.0	—
South American	—	—	13.2	96.7– 98.9	—	43.5
Mamaroneck, New York	—	36.0–42.0	7.1	90.0–110.0	18.0 36.0	—
Average	0.940	39.1	11.7	92.0–105.6	22.0–32.4	42.8

forerunnings, and the zoösterols come over when the distillate solidifies[180]. When the hot liquid zoösterol fractions are poured into a stirred cold mixture of equal parts of acetone and methyl acetate and cooled gradually to 15°C, pure white crystals of *cholesterol* may be filtered off.

Products Distilled from Wool Grease. Wool grease varies in composition according to whether the suds from wool scouring are kept separate or are mixed with the soap suds from the scoured woolen goods in the woolen mills, where the wool is washed, spun, and woven; in the Bradford area of England approximately 14,000 tons of grease a year are scoured from raw wool and recovered. About one-third of the wool grease is recovered by the wool combers themselves, and two-thirds is dumped into the sewers from a large number of small wool-combing firms in that area by arrangement with local authorities. The *sewage grease* amounted to 9000 tons in 1940, and its economic disposal presented a problem.

Low grades of wool grease of the kind described, such as sewer grease, can be used in the dry distillation of what is known in the trade as *wool fat olein* (an oil), *olein-stearin* (a semi-solid fat) and *wool fat stearin* (stearin pitch). The distillation process is conducted with superheated steam at 300–350°C. The grease itself was generally recovered by first acidifying the effluent, filtering the sludge hot, and allowing the filtered grease and liquor to separate. The distilled *wool olein* consists of 40 to 66 per cent liquid fatty acids, and the remainder unsaponifiable matter; it is used as a spinning oil but otherwise the demand is limited. The olein-stearin, or *wool stearin*, consists of 16–33 per cent unsaponifiable and the balance fatty acids; it has a melting point below 45°C, and is used as soap stock for which

there is a ready market. *Stearin pitch* consists of 32 to 57 per cent unsaponifiable, and the remainder fatty acids. Its melting point is over 45°C and it is used as a filling material for leather, impregnating waterproof materials and paper, and in the textile industry.

Chemical Constitution of Wool Grease. Wool grease consists largely of carboxylic esters of zoösterols and saturated aliphatic alcohols, a small amount of free sterols, free acids, lactones and hydrocarbons. The acid components of the esters consist largely of acids with a methyl side chain, which have been termed *lano-* and *agno*-acids, together with some normal chain and mixed hydroxy acids. The earlier chemical literature refers only to "lano acids" and their properties. They were not definitely isolated in a pure condition until the advent of improved distillation technique employed by Weitkamp in 1945. This investigator has listed a series of *normal acids*, *iso-acids* (lano-acids), and *anteiso acids* (agno-acids), all isolated from wool grease (degras).

In 1937 Heiduschka and Nier[99a] separated 62.7 per cent of fatty acids (inclusive of about 11 per cent free fatty acids), 32.8 per cent unsaponifiable matter and 1.1 per cent of ether-insoluble constituents. Kuwata and Ishii[148], by a method involving saponification, extractions with selective solvents, and fractional distillation conducted at 4 to 7 mm pressure, had obtained in 1936 both liquid and solid acids, the latter C_{14}, C_{16}, C_{18}, C_{20} and C_{21}. From their chemical behavior he concluded that they were not normal chain acids and this led to the establishment of the so-called "lano series": *lanomyristic*, *lanopalmitic*, *lanostearic*, and *lanoarachidic acids*. Lanostearic acid, for example, had a recorded melting point of 54–56°C. This acid, however, in its purified state—namely, one with a methyl side chain group in the penultimate position—Weitkamp found to have a melting point of 69.5°C. It is now known that the lano acids of Kuwata and Ishii were mixtures of iso-acids and anteiso-acids, the latter with the methyl side chain in the antepenultimate position.

Acid Components of Estolidic Esters. In Weitkamp's investigations[315] 32 acid components were isolated from the sterol esters separated from a lot of "centrifuged degras" purchased in 1941 from a concern in Boston, Mass. He used a laboratory vacuum still identical with that described by Weitkamp and Brunstrum[316] in 1941, except for the substitution of a more efficient spiral-conical pattern of wire gauze packing[317]. The packed section was 44 inches in length by one inch in diameter. The over-all efficiency was approximately 100 theoretical plates. The degras contained moisture 1.2, free acids 11.05, combined acids 44.05, and unsaponifiable (sterols, etc.) 46.1 per cent. By a new method of structure elucidation he was able to recover 4 homologous series of acids.

I. Series of *normal acids* with the structure:

$$CH_3—(CH_2)_{2n}—COOH \qquad n = 4 \text{ to } 12 \text{ inclusive}$$

The normal acids isolated were *capric* (m. 30.9°C), *lauric* (m. 42.9°C), *myristic*, *palmitic*, *stearic*, *arachidic*, *behenic*, *lignoceric*, and *cerotic*. Synthetic normal acids, *n*-decanoic (m. 31.19°C), *n*-dodecanoic (m. 43.75°C) etc., have melting points a trifle higher, but this they believed to be due to slight impurities in the natural acids. Of the normal acids C_{16}—C_{24}, only palmitic and stearic have been found in appreciable amounts.

Weitkamp has also shown that the iso-acids recognized by Kuwata and Ishii[118] do have a methyl side linkage in the penultimate position, that is, they are of the following structure:

II. $$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—(CH_2)_{2n}—COOH \qquad n = 3 \text{ to } 11 \text{ inclusive}$$

The members of the iso-acid series in degras are *isocapric* (liquid), *isolauric* (m. 41.2°C), *isomyristic* (m. 53.3°C), *isopalmitic* (m. 79.4°C) *isostearic* (m. 69.5°C), *isoarachidic* (m. 75.3°C), *isobehenic* (m. 79.4°C), *isolignoceric* (m. 83.1°C), *isocerotic* (m. 86.9°C), and *isomontanic* (m. 89.3°C). The solid iso-acids crystallize in thin plates appearing as elongated parallelograms with a characteristic profile of about 75; the higher numbers appear to the unaided eye as fine needles.

The general structure of the hydroxy acids referred to by Weitkamp is:

III. $$CH_3—(CH_2)_{2n-1}—\underset{\displaystyle OH}{\underset{|}{CH}}—COOH \qquad n = 6 \text{ to } 9 \text{ inclusive}$$

Note: The hydroxy acids have been isolated by Noxoe in both the iso- and anteiso- forms (see p. 133). In wool grease technology they are referred to as hydroxy*lano*- and hydroxy*agno*- acids respectfully.

The identities of the so-called *lano*-acids had remained obscure until the isolation of the *anteiso acids* from the estolidic esters of *degras* (wool grease origin) of Weitkamp[115]. The structure assigned to the *anteiso* series is

IV. $$CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—(CH_2)_{2n}—COOH \qquad n = 2 \text{ to } 13 \text{ inclusive}$$

The methyl group is in the antepenultimate position, which results in lower melting points for these acids than are obtained with the iso-acids which have the CH_3 group in the second instead of the third position. The *lano*-acids have melting points which indicate that they are mixtures of both the *iso*-(true lano-) and *anteiso*-acids (agno-acids).

Velick and English[300a] synthesized the anteiso acid, *d-14-methylpalmitic acid* and compared its configuration with the natural acid from "wool fat." The synthetic product melted at 36–36.8°C, the natural product at 37.3–37.8°C. The optical rotation of the synthetic product wax $[\alpha]_D^{29}$ was 5.16°, natural $[\alpha]_D^{26}$ 5.23°; the long crystal spacing was 32.8 Å for each.

TABLE 30. THE ANTEISO-ACID CONSTITUENTS OF DEGRAS—BY WEITKAMP[315]

Carbons	Antieso-acid	M.P. (°C)	Comparative % Yield of Me Ester	$[\alpha]_D^{25}$
(9)	6-Methyloctanoic	liquid	0.1	
(11)	8-Methyldecanoic	−18.5	0.6	
(13)	10-Methyldodecanoic	6.2	1.0	
(15)	12-Methyltetradecanoic	23.0	4.8	4.7
(17)	14-Methylhexadecanoic	36.8	3.6	5.0
(19)	16-Methyloctadecanoic	46.8	4.8	4.6
(21)	18-Methyleicosanoic	55.6	5.6	
(23)	20-Methyldocosanoic	62.1	3.6	
(25)	22-Methyltetracosanoic	67.8	7.0	
(27)	24-Methylhexacosanoic	72.9	5.2	
(31)	28-Methyltriacontanoic	80.7	1.0	

If the alkane side linkage is in any position except the terminal one the acid is optically active, and there are three forms known as DL, D (levo), and L (dextro). These optically active acids differ in melting point and crystal spacing and rotatory power, for example, 13-methyltetracosanoic acid:

	M.P. (°C)	Crystal Spacing (Å)	$[\alpha]_D^{25}$
DL	68.4–68.6	34.2	
D (levo)	65.4–65.6	33.0	3.46°
L (dextro)	65.4–65.6	33.0	−3.46°

Crystal spacings of iso acids from wool grease, and also anteiso acids, and of their corresponding amide derivatives have been given by Velick.[300a].

LONG SPACING (Å) OF ISO-ACID

	of Acid	of Amide
12-methyltridecanoic	26.8	27.0
14-methyltridecanoic	30.7	28.8
16-methyltridecanoic	33.8	35.0
17-methyltridecanoic	36.2	36.9
18-methyltridecanoic	37.8	36.8
20-methyltridecanoic	41.4	39.9
24-methyltridecanoic	48.4	48.3

LONG SPACING (Å) OF ANTEISO-ACID

	of Acid	of Amide
d-12-methyltetradecanoic	—	29.2
d-14-methyltetradecanoic	33.4	32.8
d-16-methyltetradecanoic	34.2	25.8

Note: Observed side spacings for iso-acids were D_1 4.39–4.60, D_2 3.74–3.78, D_3 2.32–2.33. For more complete tables consult original reference[300a].

In 1952 Tiedt and Truter[274a] of the University of Leeds, England, separated the agno-acids, *26-methyloctacosanoic acid* (m. 76.1°, $[\alpha]_D^{18}$ ($CHCl_3$) + 1.8, amide m. 102.8°C), *24-methylhexacosanoic* ($[\alpha]_D^{18}$ +1.5), and *28-methyltriacontanoic* ($[\alpha]_D^{18}$ +3.0) from the cholesteryl esters of woolwax. The isolation of the C_{29} agno-acid (m. 76.1°C) completes the series of anteiso-acids in woolwax.

Hydroxy Acids in Wool Grease. In 1942 Nozoe[200] isolated several hydroxy acids from wool grease. They were identified as alpha acids, and found in both DL and L optical forms. In his investigation he treated a benzene solution of wool grease with sodium methylate for 10 hours and then distilled the alcoholized product under 0.5 mm pressure. The "fraction below 220°C" was saponified with alcoholic KOH after removal of a benzene-soluble part. This was then esterfied with methanol and H_2SO_4. The ester was dissolved in benzene, filtered through an aluminum oxide layer, washed with benzene and extracted with ethanol-benzene (1:1) for 3 days. The extract was distilled under low pressure to remove the solvents; washed with hot water and redistilled to completely drive off the benzene. The yield was 27 grams of yellow semisolid mixture of hydroxylated fatty acids from 2 kilograms of wool grease. The acids identified were DL- and L- forms of α-hydroxy C_{12} to C_{16} acids, and α-hydroxylano C_{18} and C_{20} acids.

By treating the "fraction below 250°C" with a modification of the procedure above outlined, Nozoe obtained white crystals of mixed hydroxylanolic acids (m. 57°C yield 35 g) from which were isolated:

α-hydroxylanomyristic (m. 66°C), α-hydroxyagnomyristic (m. 40°C).
α-hydroxylanopalmitic (m. 72°C), α-hydroxyagnopalmitic (m. 54°C).
α-hydroxylanostearic (m. 77°C), α-hydroxyagnostearic (m. 65°C).
α-hydroxylanoarachidic (m. 80°C), and α-hydroxyagnoarachidic (m. 71°C) acids.

Earlier investigators, Darmstädter and Lifschütz[65], and Kuwata and Ishii[148] had reported the presence of a hydroxy C_{16} acid, which was termed *lanopalmic*, or *lanopalminic* acid. The acid (content of 7 % in mixed acids)[147] was described as consisting of white needles having a melting point of 86–87°C, and an optical rotation $[\alpha]_D$ of +523 in chloroform. It was possibly a mixture of α-hydroxypalmitic acid (m. 93.5°C) and a very small percentage of isomers.

According to Horn and associates[110a] of the National Chemical Research Laboratory, Pretoria, South Africa, nearly 30 per cent of the acid fraction of wool grease from merino fleeces is composed of hydroxylated fatty acids. They found that the α-hydroxystearic acid fraction was a mixture of isomers with 16-methyl-2-hydroxyheptadecanoic (α-hydroxylanostearic) as the main component and *n*-α-hydroxystearic acid as the probable second component. These investigators report α-hydroxypalmitic acid (m. 93.5°C, $[\alpha]_D^{cf.}$ −3.2) to constitute 18.8 per cent of the acid fraction. The amount of

α-hydroxylauric (m. 78–78.5°C, $[\alpha]_D^{cf.}$ −2.8) and α-hydroxystearic (m. 76.5–77.5, $[\alpha]_D^{cf.}$ 3.8) acids amount to 0.6, 3.8, and 4.6 per cent, respectively.

Tiedt and Truter[274a] have recently separated a C_{32} hydroxy acid (m. 95.4–96.6°C) from woolwax esters, indicating that there may be still other hydroxy acids in the high molecular range.

Kuwata and Ishii[148] isolated a dihydroxy acid (m. 103–105°C), which was termed *lanoceric acid*; it was later encountered by Lipson[166]. Its formula has been given as $C_{32}H_{64}O_4$, although it may be *threo*-dihydroxytriacontanoic acid, $C_{30}H_{60}O_4$.

Bertram[25] states that combined hydroxy acids have been shown to be the most characteristic and important components of woolwax. Both American and Australian woolwaxes were found to contain large proportions of diestolidic esters of the alcohols of the unsaponifiable fraction. Weitkamp[315] found 4 per cent of *hydroxypalmitic acid* in the estolidic esters of "degras." Darmstädter and Lifschütz[65] in 1896 had found 7 per cent of the same acid in woolwax separated from the scouring liquor of merino sheep wool, although their acid was probably impure. Weitkamp[315] isolated 0.2 per cent of the α-hydroxy C_{14} acid, namely 2-*hydroxytetradecanoic*, also optically active.

J. Radell and his co-workers at the Eastern Regional Research Laboratory, Philadelphia, Pa., have reported [*J. Am. Chem. Soc.*, **76**, 4188 (1954)] on the isolation of a new fraction from woolwax acids. By the saponification of woolwax and the isolation of the acid fraction (52.2%) it has been possible to separate chromatographically from the "acid" fraction a nonacidic material which appears to be a lactone of molecular formula $C_{20}H_{38}O_2$ representing 12 per cent of the acid fraction (or 6.3 % of the original lanolin). Infrared examination of the lactone dissolved in carbon disulfide showed a carbonyl absorption band which agrees with that for a δ-lactone carbonyl. Such a compound would explain the difficulty encountered in obtaining woolwax acids free from any appreciable saponification number. Furthermore, these investigators state that the presence of a δ-hydroxy acid in woolwax acids is indicated, although thus far the only hydroxy acids isolated from woolwax were α-hydroxy acids. The δ-lactone has a saponification equivalent of 311.1, specific rotation of $[\alpha]_D^{20}$ + 13 ($CHCl_3$, c = 4), and a molecular weight (cryoscopically in benzene) of 316.

Sterols in Woolwax. Lipson[166] extracted woolwax (acid value 4.94, iodine number 33.5) from the base of the fleece, and attempted to separate the wax components by chromatographic analysis, in which he used a column of alumina, and selectively adsorbed the woolwax components from a petrolic ether and benzene solution. The alumina adsorbed 21 per cent of wax, with the free fatty acids at the top, 6 per cent of free sterols (choles-

terol and lanosterol) half-way down, and unidentified products, probably esters of higher fatty alcohols, at the bottom.

Saponification of the unadsorbed filtrate ostensibly gave *lanoceric acid*, $C_{32}H_{64}O_4$, and *lanosterol*, $C_{30}H_{51}(OH)$? (m. 140–141°C), with a small percentage of *cholesterol*, but says Lipson that there is no *agnosterol*. It is of interest to note that Kuwata and Ishii[143] based their formula of lanoceric acid on a potassium (K) content of 7.17–7.20 per cent of the K salt of the acid, and the formation of a lactide, $C_{64}H_{122}O_5$ (m. 98.5–99°C) when the K salt is boiled with concentrated hydrochloric acid.

Woolwax is rapidly and completely saponified by either NaOH or KOH in aqueous alcohol. For example, Barnes and his co-workers[20a] added molten woolwax to a 4 per cent NaOH solution in 90 per cent ethanol, and after stirring and refluxing for 40 minutes, a sufficient amount of water was added to give a water-ethanol ratio of 2; then the woolwax alcohols were extracted repeatedly with petrolic ether. The yield of total alcohols was 44 per cent. Acidification of the soaps yielded 56 per cent of fatty acids.

Of the alcohols about 20 per cent are of steroid structure, (sterols and triterpene alcohols), leaving about 24 per cent of straight-chain alcohols. Tiedt and Truter[274a] have isolated (by separation of urea adducts) five normal alcohols, namely octadecanol, eicosanol, docosanol, tetracosanol, and hexacosanol. They constitute about 1 per cent of woolwax. They also encountered secondary alcohols to the extent of 1¾ per cent. No evidence of alcohols of higher molecular weight was found.

The unsaponifiable of woolwax contains 29 per cent of crude cholesterol (by digitonin estimation), or 12.3 to 9.5 per cent on the basis of the original grease. The monohydric long-chain alcohols were described as *cetyl* (C_{16}), *lano-octadecyl* (C_{18}), *carnaubyl* (C_{24}), and *ceryl* (C_{26}), before the elucidation of a complete series of anteiso- and iso- alcohols by Murray and Schoenfeld[195a]. The starting material used in their study was extracted with trichloroethylene from a bale of authentic merino sheep wool. They removed the triterpene alcohols from the unsaponifiable by virtue of their low solubility in methanol. Cholesterol was separated as its addition compound with anhydrous zinc chloride. After the triterpene alcohols were filtered off and the cholesterol separated, the residual alcohols (80.6 per cent) were reacted with acetic anhydride, purified and fractionally distilled.

For the distillation, a column of the spinning band type of Murray, which has a lower pressure drop than the Stedman type used by Weitkamp, was chosen, since it permits normal alkyl acetates up to C_{34} to be distilled. The alcohols were then obtained by saponification of the acetates. In this manner these investigators were able to isolate an anteiso- series of alcohols ranging from C_{17} to C_{27}, and an iso-series ranging from C_{20} to C_{26}. The anteiso- alcohols show optical rotations ($[\alpha]_D^{23}$, in $CHCl_3$) of 4.4 to 3.5.

Tiedt and Truter[274a] have reported the presence of *n*-alcohols of even carbon number from C_{18} to C_{26}.

Anteiso-series	M.P. (°C)	Iso-series	M.P. (°C)
14-Methyl hexadecanol	18.4	18-Methyl nonadecanol	50.3
16-Methyl octadecanol	27.5–31	20-Methyl heneicosanol	57.1
18-Methyl eicosanol	40.1	22-Methyl tricosanol	62.4
20-Methyl docosanol	48.5	24-Methyl pentacosanol	67.2
22-Methyl tetracosanol	54.6		
24-Methyl hexacosanol	61.0		

Murray and Schoenfeld[195] found small proportions of high-melting diols, e.g., 1,2-alkanediols, reported previously by Horn and Hougen[110]. Apparently they are within the range of C_{16} to C_{24}, and have melting points ranging from 69 to 85°C, and have been estimated to form 1.5 per cent of the original unsaponifiable. Of the aliphatic alcohols, 3 per cent are below C_{17}, and 4 per cent above C_{27}. Eighty-five per cent are within the C_{20}–C_{27} range.

Murray and Schoenfeld have recently reported [*Austr. J. Chem.*, **8**, 424–431 (1955)] seven *n*-alcohols which were isolated from the unsaponifiable part of a Merino woolwax and identified as *n*-$C_{18}H_{37}OH$; *n*-$C_{20}H_{41}OH$; *n*-$C_{22}H_{45}OH$; *n*-$C_{24}H_{49}OH$; *n*-$C_{26}H_{53}OH$; *n*-$C_{28}H_{57}OH$; and *n*-$C_{30}H_{61}OH$. These *n*-alcohols were estimated to comprise 2–3 per cent of the unsaponifiable fraction. The order of decreasing amounts was C_{26}, C_{24}, C_{28}, C_{22}, C_{30}, C_{20}, and C_{18}.

The chief sterol (9 per cent of woolwax) is *cholesterol* [$C_{27}H_{45}(OH)$, m. 147–150°C, $[\alpha]_D$ −29.5°C]. Heidushcka and Nier[99a] in 1937 reported the presence of a steroid which they termed *isocholesterol* (m. 135–137°C). Some years later Ruzicka and his associates proved the so-called *isocholesterol* to be a mixture of steroids (actually pseudosterols) having a greater number of double bonds than cholesterols. These nonemulsifying pseudosterols (namely triterpenoid alcohols) are lanosterol, $C_{30}H_{61}(OH)$, and agnosterol, $C_{30}H_{49}(OH)$. Lanosterol, as first isolated, was later resolved as a mixture consisting of *lanosterol*, $C_{30}H_{52}O$, *dihydrolanosterol*, $C_{30}H_{50}O$, and γ-lanosterol. Dihydrolanosterol is believed to be identical with *agnosterol*, or closely related to it.

Knol[183], in his review of the aliphatic woolwax alcohols, states that "it is striking that the percentages of aliphatic alcohols which could be isolated from the unsaponifiable part of woolwax in different ways are in close agreement: Truter about 20 per cent, v. Rudloff, 21 per cent and Murray and Schoenfeld, 22.5 per cent. Taking into consideration that the sterols form about 30 per cent of the unsaponifiable matter and the "triterpene alcohols" about 25 per cent, there remains an unknown of about 25 per cent, which needs further investigation."

Unlike ordinary sterols, lano- and agnosterol are not precipitated by digitonin and are not emulsifying agents. Their structures are not known with certainty; it was believed that they might have the "picene" skeletal structure of tetracyclic terpenes, but it is now postulated that they have a pentacyclic structure with an isopropylidene end group to a pentagonal member of a five-ring structure, with an OH group adjacent to two methyl groups, similar to lupeol (see p. 31).

Lanosterol has two double bonds. There are several isomeric or related forms, including γ-lanosterol, $C_{30}H_{49}(OH)$ (m. 141°C), as discovered by Bellamy[20b]. The probable site of the biosynthesis of these triterpenoid alcohols is said to be the sebaceous glands. *Agnosterol*, $C_{30}H_{47}(OH)$ (m. 163.5–164.5°C), has three double bonds. It is of the type formula $C_nH_{2n-13}(OH)\cdot H_2O$ to which ergosterol belongs, but is of a different ring structure. Only a trace of *ergosterol*, $C_{28}H_{43}(OH)\cdot H_2O$ (m. 165°C), has been found in woolwax.

The esterified alcohols in woolwax (lanolin) have good emulsifying properties. The relatively low melting points of the cholesterol and isocholesterol estolidic esters in woolwax are apparently caused by their close chemical relation to the anteiso- acids, which have comparatively low melting points.

In 1945 Daniel, Lederer, and Velluz[64a] of the University of Lyon, dissolved the unsaponifiable fraction of wool fat in petrolic ether and passed it through a column of alumina. The first filtrate contained a very small amount of a mixture of paraffin hydrocarbons. Successive fractions obtained by adsorption and elution contained: (1) a very small amount of unidentified unsaturated *d*-rotatory steroid ketones; (2) cholesta-3,5-dien-7-one, strongly *l*-rotatory, about 0.6 per cent of the original lanolin; (3) "isocholesterol" (a mixture of lanosterol, dihydrolanosterol, γ-lanosterol, and agnosterol), 20–26 per cent; (4) cholesterol, 20–30 per cent; and (5) a mixture of dextrorotatory substances amounting to 5 per cent. Substance (2) does not exist as such in lanolin; it is formed from esters of 7-ketocholesterol during saponification. Lanolin also yields 2 to 6 per cent of β-cholestanol. Isocholesterol as well as cholesterol is present in the hair fat of the sheep, goat, llama, and dromedary.

Commerical woolwax yields about 2 per cent of combined dihydric alcohols (diols) and as high as 4 to 5 per cent from merino fleece. It is believed that the principal natural diol has a single methyl branch in the alkyl chain, iso- and anteiso-C_{18} diols. The natural diol was similar to but not identical with *octadecane-1,2-diol* prepared synthetically, according to Horn and Hougen, of the South African Council Scientific Industrial Research, Pretoria[110].

Commerical Cholesterol and Lanolin Acids. Cholesterol is the best known and the most readily available of the sterols; it is the typical sterol of the

TABLE 31. CHEMICAL COMPOSITION OF COMMERCIAL WOOL GREASE

Neutral, Iodine No. 35

Cholesteryl and Isocholesteryl Estolidic Esters:	32.5–33%
Cholesterol, 9%	
7,8-Dihydrocholesterol, $C_{27}H_{47}OH$ (m. 143°C), small amt.	
Isocholesterol (lanosterol and agnosterol), 6–7%	
Carboxylic acids, 16–18%	
Branched chain (mostly anteiso)	
Hydroxylated acids, 4–5%	
Free Sterols:	0.8–1.5%
Cholesterol	
Dihydrocholesterol	
Free Triterpenoid Alcohols:	4.5–5.5%
Lanosterol (m. 140–141°C), 4½%	
Agnosterol?	
Esters of Aliphatic Alcohols with Fatty Acids:	48–49%
Combined fatty acids (m. 41.8°C, m. wt. 327.5), 27%	
n-Carboxylic acids, principally C_{16}–C_{26}, 5–6%	
Isocarboxylic acids (lano-acids) C_{17}–C_{26}, principally C_{20}–C_{26} (all even C), 4½%	
Anteisocarboxylic acids (agno-acids), C_9–C_{31}, principally C_{15}–C_{27}, 12–13%	
Hydroxylated normal, lano- and agno- acids, 4–5%, C_{17}–C_{32}, principally C_{16}–C_{24}	
Combined alcohols (m. 33°C, m. wt. 239), 20–22.5%	
Saturated monohydric alcohols (C_{16}–C_{26}) normal, iso-, and anteiso-	
Unsaturated monohydric alcohols (C_{16}–C_{12})	
Saturated dihydric alcohols (C_{16}–C_{24}), 2–3%	
Free Fatty Acids:	3–7%
C_{16}–C_{26} (neutr. val. 170)	
Lactones of Hydroxy Acids:	6–6.5%
∂-Lactone, $C_{20}H_{28}O_2$, mol. wt. 316	
Mineral Matter (as K_2O):	0.5%
Hydrocarbons:	1–2%

vertebrate animals. It serves as the major source material in the manufacture of hormones and of vitamin D_3. Cholesterol is obtained from the brains and spinal cords of cattle, which contain 10 per cent of their dry weight as free cholesterol. It is obtainable from the waste of shrimp canneries. Anhydrous lanolin (woolwax) is an important source, although a problem is involved in competely separating it from isocholesterol (see p. 139). Cholesterol ordinarily crystallizes from anhydrous solvents in the form of needles or prisms, and from 95 per cent ethanol as plates containing one mol of water. It is very soluble in hot ethanol, but less than 1 per cent soluble in cold ethanol (96 per cent); it also dissolves freely in both chloroform and ether.

(1) A Dutch patent[72] claims that cholesterol and isocholesterol may be precipitated from a dispersion of 1000 g of wool grease (29 per cent cholesterol) in 100 ml of

ethanol by a solution of calcium chloride. This solution is made up from 180 g of the dry calcium chloride in 500 mg of ethanol; it is poured into the wool grease dispersion and the whole left standing for 24 hr at room temperature. 4000 ml of acetone is added and the precipitate removed, washed with acetone, and dried. The crude product amounts to 465 g with a so-called "cholesterol" content of 44 per cent, and the yield is 70 per cent of theoretical. Water (2000 ml), when added to the remaining solution, will precipitate a crude product with a 55 per cent "cholesterol content," so that the sterols can be completely recovered.

On distillation under 3 mm pressure at 270–310°C of the unsaponifiables (woolwax alcohols) of the wool grease, of the grease itself, or of the dry saponification product, the triterpene and lower aliphatic alcohols are obtained as forerunnings; the cholesterol comes over when the distillate solidifies. The hot liquid cholesterol fractions are poured into a stirred cold mixture of equal parts of acetone and methyl acetate and cooled to 15°C, when pure white crystals of cholesterol may be filtered off[72].

(2) Isocholesterol can also be obtained by fractionally distilling *in vacuo* the *steroids of the unsaponifiable matter* from wool grease, or lanolin, with the aid of superheated steam or gas, to yield a fraction which contains about 40 per cent of isocholesterol. The fraction is dissolved while still hot in a mixture of benzene and acetone in which cholesterol is very soluble, and the solution then cooled to crystallize out the isocholesterol.

(3) Anhydrous lanolin is rapidly and completely saponified by either NaOH or KOH in aqueous ethanol. On a practical scale 10 gal of a 4 per cent KOH solution in 90 per cent aqueous ethanol is refluxed, stirred, and 35 lb of molten lanolin added in the course of 15 min. After stirring and refluxing for a further 40 min., water is added to give a water-ethanol ratio of 2. The woolwax alcohols can be extracted with 20-gal portions of petrolic ether. Seven such fractions, according to Barnes *et al.*[20a], yielded a total of 15.5 lb of alcohols (44 per cent of basis weight). Acidification of the soaps gave 19.56 lb of fatty acids.

(4) Isocholesterol is nearly insoluble in methanol at 40°C, whereas cholesterol is 1.88 per cent soluble. Thus, according to Hewett[103a], the unsaponifiable components of wool grease (1000 g) can be dissolved in boiling methanol (7000 g) and the solution cooled to 40°C, when the "isocholesterol" will separate. The crude isocholesterol is filtered off and recrystallized from methanol (4000 g). The combined methanol filtrates are evaporated to dryness and the residue is dissolved in dimethylketone, $CO\,Me_2$ (4000 g), and after cooling overnight a wax like compound (100 g) separates and is removed by filtration. The $CO\,Me_2$ liquors are evaporated to dryness and the residue is dissolved in glacial acetic acid (1000 g). On cooling, cholesterol (165 g) is obtained as needles (m. 148–149°C) after recrystallization from the methylated spirit. If the preliminary removal as isocholesterol is omitted, the separation of cholesterol and isocholesterol is effected by filtering the acetic solution at 30–35°C, thus retaining the isocholesterol in solution.

Drekter and Conrad[70] have described a method by which isocholesterol may be isolated from wool grease by saponifying the wool grease with an aqueous solution of barium hydroxide at a temperature below its boiling point. The resultant isocholesterol product is washed with water, the residue is dried, and is extracted with a hot solvent (acetone), from which isocholesterol precipitates on cooling. For the recovery of free cholesterol, the solution remaining after removal of the isocholesterol may be treated with methanol. The methanol solution is then separated from insoluble material and dried, and the residue dissolved in hot 95 per cent ethanol, forming a solution from which the cholesterol crystallizes on cooling.

The commercial lanolin acids obtainable as a by-product in the saponification of woolwax to obtain cholesterol are of commercial utilization. The lanolin acids and derivatives (e.g., soaps) are used as wetting and emulsifying agents (oil-in-water type), in catalysts in petroleum cracking, as bases for pharmaceuticals, in modelling compounds, etc. Sulfonated derivatives are recommended for the treatment of leather[170a].

Woolwax Alcohols. Woolwax alcohols or lanolin alcohols, extensively employed in cosmetics and medical ointments, were introduced into the British Pharmacopœia in the 6th Addendum. They are usually obtained by the saponification of wool grease or lanolin followed by the extraction of the alcohols from the soaps. The yield of alcohols by this method is about 50 per cent of the raw material. The Wool Research Associates[170] gives the following specifications for a select grade known as "Hartolan": ash 0.2 to 0.3 per cent, soap 1.8 to 2.5 per cent, ester value 2.0 to 4.3, acid value 1.5 to 2.5, acetyl value 128–133, iodine number (Wijs) 44 to 45.2, melting point 60–61°C, *cholesterol* 28.2–34.1 per cent, *isocholesterol* 10.8 to 12.9 per cent. This grade has a mean molecular weight of 377, pH value 5.7, saponification number less than 8, flash point 393°F, fire point 474°F, viscosity at 200°F (Redwood No. 1) 32 seconds, unsaponifiable matter 96–98 per cent, specific rotation—11.8°. The material has a brownish-yellow, waxlike structure, and is very brittle at 10°F. It does not become rancid.

Eisner *et al.* find that the acids, in the form of esters, in wool grease on reduction by sodium and methylisobutyl carbinol are converted to alcohols similar to the aliphatic alcohols obtained by saponification. They state that the sodium reduction process can be satisfactorily applied to all grades of wool grease, and in this respect is superior to the hydrogenolysis of lanolin described by Fayoud and Rivera. A useful mixture of alcohols can be prepared, as an alternative to saponification, and with a yield of 80 per cent. The difference in the sodium-reduced product is that it contains more aliphatic alcohols.

In general the product obtained from the sodium reduction of woolwax is a semi-soft, cream-colored solid, waxlike in appearance and slightly tacky to the touch. The product similarly obtained from the technical greases is light brown and quite odorless. Both contain 1,2-diols as a result of the reduction of hydroxy acids present in the raw material. The sodium-reduced lanolin has a refractive index of 1.474 at 60°C, acid number 0.5, ester number 3.9, and per cent hydroxyl 4.93. In comparison, USP lanolin has a refractive index 1.475 at 60°C, acid number 1.2, ester number 95.4, per cent hydroxyl 1.22. These investigators also report that sodium-reduced lanolin contains 25.4 per cent cholesterol, and 19.9 per cent lanosterol; whereas the alcohols prepared by saponification contain 39.1 per cent cho-

lesterol, and 27.1 per cent lanosterol. The reduced lanolin dissolves more readily in mineral oil, an advantage in some cosmetic formulations. [Eisner, A., Scanlan, J. T., and Ault, W. C., *J. Am. Oil Chemists' Soc.*, **32**, 556–558 (1955).]

Woolwax alcohols, according to Lower,[170] have the following applications: adhesive plasters, emulsifying agents, ointment bases, artificial bile injections, suppositories, in leprosy treatments and antirachitic preparations, cosmetic preparations, biological creams, sun-tan preventives, hair bleaches, vitamin and hormone preparations. An example of the latter is estrogenic hormone cream.

SOLID MARINE ANIMAL WAXES

Spermaceti

Spermaceti is a wax found in the head cavities of the sperm whale, *Physeter macrocephalus* Linné (*P. catadan*), which is the largest of the toothed whales or cachalots. Spermaceti also occurs to a much lesser extent in the blubber oil of the sperm whale, and in the bottlenose whale, *Balaena rostrata*[274] and a few other cetaceans, but not in the oil of whalebone whales.

The sperm whale is 60 to 80 feet in length, with an enormous head, 30 feet in circumference, in which there is a large hollow on the upper surface of the skull, filled with a peculiar fatty tissue. When the spongy mass is removed from the head, the oil is allowed to separate by draining. Spermaceti is in the oil in a dissolved state while the animal is living, but tends to concrete later on. The resultant mass, after draining the oil, is boiled in a 2 to 3 per cent lye solution to clean it; it is then washed free from alkali, and the wax melted and moulded into cakes.

One sperm whale yields upward of three tons of oil and over 500 pounds of spermaceti. The blubber oil can be hydrogenated to obtain a spermaceti wax that is a trifle harder and higher in melting point (46–50°C) than the natural spermaceti (m. 43–47°C). In the refineries the strained oil is allowed to stand in refrigerators for several days at a temperature of 0°C (32°F), and then pressed to produce what is known as "stearine-free" oil (see Sperm p. 146). Spermaceti is also recovered from the press residues by re-pressing at a higher temperature.

Spermaceti is white, somewhat translucent, in slightly unctuous masses of a scaly, crystalline fracture and pearly luster, with a very faint odor, and a bland, mild taste. It becomes yellowish and somewhat rancid on long exposure to air[294].

Properties of Spermaceti. Since spermaceti has in the past been adulterated with paraffin or other substance, considerable attention has been given by cosmetic and pharmaceutical authorities to the promulgation of suitable standards of physical and chemical constants to define its

purity. One of the early references concerning the specific gravity of spermaceti was that of Kebler[128], who examined twenty samples of spermaceti and found the specific gravity (d^{15}) to range between 0.905 and 0.945. The German Pharmacopoeia V favored limits of 0.940 to 0.945 at 15°C. The present spermaceti of commerce has a specific gravity of 0.938 to 0.944 at 25°C, and of 0.842 at 100°C. Ullmann[228a] gives the specific gravity range as 0.943 to 0.960 at 15°C. DeNavarre[66a] gives the limits for cosmetic purposes as 0.905 to 0.959 at 60°F.

The refractive index (n_D^{70}) of spermaceti is 1.4397[219], or almost identical with that of *cetyl palmitate*, its principal constituent. Spermaceti is soluble in hot acetone and alcohol, in carbon tetrachloride, chloroform, ether, naphtha, and turpentine. It has an acid value 2–5.2, saponification number 108–134, iodine number 4.8–5.9, and unsaponifiable 51–53.8 per cent. DeNavarre[66a] gives the acid value 0–1.8, iodine number 3–4, and saponification number 122.6–135 for a cosmetic grade. Spermaceti, when subjected to excessive heat (pyrolysis), is partially converted into palmitic acid and cetene ($CH_2{=}CH{\cdot}CH_2(CH_2)_{12}CH_3$), which increases both the acid value and iodine number.

It is of interest to note the various melting points (°C) recorded by early investigators for pure spermaceti: Saussure 47, Chevreul 44, Stenhaus 41.6, Wimmel 44–44.5, Rüdorf 43.5–44.3, Person 42.7, Berzelius 44.7, Liebig and Bolley 44–45, Chateau and Schuhbarth 45, Bunsen 47.7, Pouillet and Müller 49, and Dulk 50.

The Fisher-Johns melting point of a specimen of pure spermaceti wax 35–38°C minimum, 40.5–41°C bulk, and 43.5–44.5°C maximum.

The U. S. Pharmacopoeia[225] specifies that the melting point of spermaceti shall come within the range 42–50°C (107.6–122°F); the British Pharmacopoeia[27] prescribed the limitations as 46–50°C (114.8–122.0°F). The usual commercial article melts at 42–46°C. Meldrum[183] observed that a sample of natural pressed spermaceti solidified at 45.75°C, always with a rise of less than 0.05°C, far less than for other waxes, even though it has a pronounced crystalline character. Solidification commences at 45.8–45.9°C, the melting point being 46°C. Meldrum also pointed out that the addition of 0.1 per cent of water, glycerol, or oleic acid has no effect on the solidifying point.

Chemical Composition of Spermaceti. The chief constituent of spermaceti is *cetyl palmitate*, which comprises at least 90 per cent. Cetyl palmitate ($C_{15}H_{31}CO{\cdot}OC_{16}H_{33}$, m.wt. 480.33), the palmitic ester of cetyl alcohol ($C_{16}H_{33}OH$), obtainable by fractional crystallization of spermaceti from alcohol, was termed *cetin* by the British Pharmacopoeia. There are also small amounts of other esters associated with cetin in spermaceti. These are believed to be myristic, lauro-stearic, and stearic esters of lauryl

cetyl, and stearyl alcohols. These alcohols were identified as early as 1854 by Heintz and termed *lethal* ($C_{12}H_{26}O$), *methal* ($C_{16}H_{34}O$), and *stethal* ($C_{18}H_{38}O$).

Cetyl palmitate melts at 51.6°C; refractive indices [n_D] are 1.4429, 1.4415, 1.4398 at 60, 65, and 70°C, respectively; 100 g of absolute ether dissolves 21.01 g of cetyl palmitate at 22°C, 2.30 g at 0°C; 100 g of absolute ethanol dissolves 0.0495 g of cetyl palmitate at 22°C. Cetyl stearate, a minor constituent of spermaceti, melts at 56.5°C, and has a refractive index [n_D^{70}] of 1.4410. It is less soluble in ether than the palmitate; 9.08 g dissolve at 22°C, and 0.73 g at 0°C. Ethanol dissolves 0.0594 g cetyl stearate at 22°C [Whitby[319]].

Reyes[229] in 1948 found that the unsaponifiable matter (approx. 55 per cent) contains 6 per cent of cholesterol, indicating that the cholesterol content of spermaceti approaches 3.3 per cent. It had been previously known that spermaceti contains 1 to 2 per cent of an unidentified fatty acid ester, and 1 to 1.5 per cent of free alcohols, including an unsaturated one. The unknown ester and alcohol constituents may now be accounted for in part as cholesteryl ester and free cholesterol. The iodine number of spermaceti freed from oil is 3.0 or thereabouts. Formerly the iodine number was ascribed entirely to the presence of oleyl alcohol.

Purity and Uses of Spermaceti. As spermaceti is occasionally adulterated with stearic acid or paraffin, or both, it is often necessary to test it for purity. Frerichs[83] recommends the following procedure.

Heat 1 g of the sample with 10 ml of aqueous ammonia in a test tube until the spermaceti is molten, shake well, cool and filter. The filtrate should yield no precipitate on addition of HCl. One per cent of stearic acid, if present, gives a distinct cloudiness. Old samples, however, are likely to give a filtrate which is milky, when the test becomes indeterminate. In order to test for paraffin it is necessary to use absolute

TABLE 32. APPROXIMATE CHEMICAL COMPOSITION OF COMMERCIAL SPERMACETI OF COMMERCE

Fatty Acid Esters:	97.5–98%
Of Monohydric Alcohols:	
Myristyl myristate (m. 38°C), less than 1%	
Oleyl myristate, oleate, and palmitoleate	
Cetyl palmitate (m. 49.2°C), 90–93%	
Cetyl palmitoleate	
Cetyl stearate (m. 55°C), 1.1–1.5%[319]	
Of Polycyclic Alcohols:	
Cholesteryl palmitate, 2–3%	
Free Fatty Acids:	0.1–0.4%
C_{15}–C_{18} acids	
Free Alcohols:	1–1½%
Cholesterol, $C_{27}H_{45}(OH)$	
Monohydric alcohols, C_{15}–C_{18}, less than 1%	

ethanol as the solvent, as well as for the determination of the acid content; 0.5 g of spermacetic must be completely soluble in 25 g of boiling absolute ethanol. The solution should not be reddened by phenolphthalein solution (absence of alkali), and should require for reddening not more than 0.1 ml of 0.1*N* KOH. Admixture with stearic acid would become immediately apparent in the test for acidity, unless the sample were a very old one. The acid value should not exceed 2, the iodine number will fall between 0 and 6, and the ester value between 116 and 133. Dunlop gives the acid value as 0 to 1.8; the saponification value 120.6 to 134.6; the iodine number of the highly purified spermaceti is 0, but values up to 9.3 (by Wijs' method) have been found, no doubt caused by the presence of sperm oil. The usual iodine number ranges from 3.0 to 5.9, and saponification number 126 to 133. The specific gravity of spermaceti may be determined rapidly by the ordinary hydrostatic method, with the aid of dilute ethanol, although accuracy of results by the method is open to question.

In medicine, spermaceti is used as a demulcent in irritations of the mucous membrane, but it has no remedial properties. An emulsion of this sort can be made by mixing spermaceti first with half its weight of olive oil, then with powdered gum arabic, and lastly with water. Spermaceti is used chiefly as a base of ointments, cerates, etc. Spermaceti Cerate (Ceratum Cetacei, U. S. Pharmacopoeia, 1890) is made by melting together 10 parts of spermaceti and 35 parts of white beeswax, and then adding 55 parts of warmed olive oil. Spermaceti is used in cosmetics, in the finishing and lustering of linens, in laundry wax, and in special soaps and emulsifying agents.

Spermaceti is used to a limited extent in the manufacture of candles, and a litle beeswax or other plastic wax is then added to make the candles less crystalline and brittle. It is important to note that spermaceti is the wax used in the candle which defines our unit of candlepower. The standard candle of Great Britain, which was also legalized in the United States, is one which weighs one-sixth of a pound and burns 120 grains of spermaceti per hour. In the manufacture of the English standard sperm candle it is prescribed by the Metropolitan Gas Referees in London that the wicks shall be made of three strands of cotton plaited together, each strand consisting of 18 threads. A number of other dimensional details are prescribed, and a careful description of the wax to be used in making the standard candle.

Spermaceti is a source of *cetyl alcohol*. It is used in cosmetics as a stiffening agent as well as for its cosmetic effect on the skin, which is not quite as pronounced as that produced by cetyl alcohol. Spermaceti is sold in blocks, or in cake form, packed in cases.

LIQUID ANIMAL WAXES

Liquid waxes are waxes which are liquid at ordinary room temperature. They consist mainly of esters of unsaturated alcohols with unsaturated fatty acids, in which respect they resemble the true waxes. They are less

dense than glycerides, of which vegetable oils are generally composed. They do not thicken or dry on exposure to air—a highly advantageous property, but they yield solid elaidins on treatment with nitrous acid. The group includes marine oils, a vegetable oil, and a bird oil.

In the marine animal waxes, solid or liquid, certain saturated and unsaturated alcohols containing 16, 18, or 20 carbon atoms per alcohol replace the glycerol found in ordinary fats and oils. Some of the liquid waxes on cooling deposit material of wax-like properties consisting largely of *cetyl palmitate*. Spermaceti is formed in this manner. In the separation of spermaceti the yield is only 10 to 15 per cent, and much of the solid wax remains dissolved in the liquid constituents.

Arctic sperm oil is a liquid wax derived from the bottlenose whale, *Hyperoodon rostratus*; it is also called *bottlenose oil* and *doegling oil*. It has very similar characteristics to sperm blubber oil of the true sperm whale or cachalot. *Dolphin oil* is a mixture of liquid wax and fat from the dolphin, *Delphinus delphia*. *Sperm oil* (sperm-head oil) is a pale-colored liquid wax from the large cavity in the head of the sperm whale, *Physeter macrocephalus* (L), and is also known as *spermaceti oil* and *cachalot oil*.

Mutton-Bird Oil

L. H. Smith[258] in 1911 stated that mutton-bird oil was the first bird oil to be put on the market. The output (from New Zealand and Tasmania) was said to be small and not likely to be of commercial importance. The oil, which is found in the bird's stomach, has a color which varies from ruby red to a clear brown, and a not unpleasant fishy smell. The sample of Smith and that of Tasmanian oil obtained years later by Evers and Foster[74] showed the following analytical characteristics:

	Smith	Evers and Foster
Color	Ruby red	Clear brown
Specific gravity	($d^{15.5}$) 0.8819–0.8858	($d^{15.5}_{15.5}$) 0.8835
Refractive index	1.4636(n_{40})	1.4712(n_{20})
Saponification number	125.9	125.9
Iodine number (Wijs)	71.0	132.0
Acid value unsaponifiable	4.6	5.7
	36.88% (m. 31°C)	31.1% (m. 32°C)
Ether-insoluble bromides (Gemmel test)	—	10.4%

The stomach oil of the mutton-bird, according to Carter[15a], contains 38.4 per cent of unsaponifiable or mixed monohydric alcohols and 61.4 per cent of mixed acids. The unsaponifiable consists of cetyl alcohol 65, oleyl alcohol 28 and cholesterol 7 per cent. The mixed acids contain 5 per cent of saturated acids; the balance is chiefly oleic acid, with linoleic acid and more highly unsturated acids, of which 12 per cent is an acid of the formula

TABLE 33. ANALYTICAL CONSTANTS OF MUTTON-BIRD OIL (1931)[9]

	Sample 1	Sample 2	Values Previously Reported
Specific gravity ($d_{15.5}^{15.5}$)	0.8880	0.8882	0.8819–0.8858
Refractive index (n_{40})	1.466	1.465	1.4636
Acid value	4.0	4.5	4.5–4.7
Saponification number	125.0	120.5	119.6–125.9
Iodine number (Wijs, 3 hr)	131.6	138.8 (Hübl, 17 hr)	71.0–132.0
Unsaponifiable	36.5%	41.7%	31.1–38.4%
Solidifying point of fatty acids	below 18°C	below 15°C	

$C_{22}H_{38}O_2$. It is believed that the commercial oil might be of value as a substitute for cod-liver oil, but this lacks confirmation. Mutton-bird oil obtained from the stomach or crop of young birds (*A. lessoni*) of New Zealand is known to contain vitamin A, and therefore may have therapeutic value.

Sperm Oil

The oils from the blubber and the head cavity of the sperm whale, *Physeter macrocephalus* L., consist of esters of higher aliphatic alcohols and acids, a large proportion of which are unsaturated in either the alkyl or the acyl radical, or both. The blubber or body oil is the far more unsaturated of the two; it is the head oil, or the more saturated one, that freely deposits on cooling the *cetyl palmitate* or *spermaceti wax* which comprises about 11 per cent of the original oil.

Sperm oil, prepared exclusively from the body blubber, is orange-red in color, and will also deposit, on chilling, an appreciable amount of crystalline solid, which may be triple-pressed for use. The oil may also be hydrogenated to produce a superior spermaceti. Toyama[277] determined the following constants on the solid portion deposited from sperm oil from the body blubber: specific gravity (d^{20}) 0.8806, (d^{30}) 0.8733; refractive index (n_D^{30}) 1.4620; acid value 1.24; saponification number 131.6; iodine number 87.4; unsaponifiable 36.4 per cent, and fatty acids 64.13 per cent. The fatty acids are orange-yellow and liquid at ordinary temperature, and have the following constants: specific gravity (d^{20}) 0.8918, (d^{30}) 0.8847; n_D^{20} 1.4602, n_D^{30} 1.4564; neutralization value 199.2; saponification number 201.8; iodine number 87.4; and ether-insoluble bromides 5.55 per cent. Sperm oil is soluble in chloroform, ether, and benzene. The cold test on the natural oil is 45°F, and that on the bleached oil is 38°F.

The fatty acids of sperm-blubber oil, according to Toyama[277], consist of about 10 per cent saturated and 90 per cent unsaturated acids. *Lauric, myristic, palmitic, stearic,* and a little *arachidic acid* comprise the saturated acids. The acids of the monoethenoid series are *zoömaric, oleic, gadoleic,* and *cetoleic*. An acid, $C_{14}H_{26}O_2$ (probably *physeteric*), is also present in small

proportion. The unsaponifiable matter of sperm-blubber oil (36.4 per cent) consists chiefly of *oleyl, cetyl* ($C_{16}H_{33}OH$) and *stearyl alcohol*, the first two predominating. Other alcohols are *cholesterol* and *glyceryl ethers* (see p. 148).

Martin[180] gives the following constants for sperm body oil: specific gravity (d^{15}) 0.880–0.883; saponification number 123–133; iodine number 81–84; Reichert-Meissl value 0.60; fatty acids 60–64 per cent, alcohols 37–41 per cent; Maumene test 45–51. It contains a large proportion of monoethenoid but no polyethenoid compounds, which are found in ordinary whale oils to the extent of about 9 per cent.

Hilditch[105] directs attention to distinct differences in the chemical composition of sperm-head oil and sperm-blubber oil. Hilditch and Lovern[106] point out that the general unsaturation is greater in blubber oil, and the average molecular weight is higher. The chief component of the alcoholic ethers in sperm-head oil is cetyl alcohol, combined largely with lower molecular weight acids (C_{10}–C_{14}). The chief component of the alcoholic ethers in sperm-blubber oil is oleyl alcohol combined with higher molecular weight acids (C_{16}–C_{22}).

Chemistry of Sperm Oil Alcohols. In 1951 Stage[258a] fractionally dis-

TABLE 34. APPROXIMATE COMPOSITION OF A TYPICAL SPERM-HEAD OIL (Hilditch and Lovern[106] and others).

Esters of Saturated Acids with Saturated Alcohols:	27%
Myristyl caprate, 4.5%	
Cetyl laurate, 5.5%	
Cetyl palmitate, 9%	
Cetyl myristate, 1%	
Octadecyl palmitate, 8%	
Esters of Saturated Acids with Unsaturated Alcohols:	24%
Oleyl myristate, 13%	
Eicosenyl eicosanate, 11%	
Esters of Unsaturated Acids with Saturated Alcohols:	8%
Cetyl physeterate	
Cetyl palmitoleate	
Cetyl lauroleate	
Cetyl myristoleate	
Esters of Unsaturated Acids with Unsaturated Alcohols:	28%
Hexadecenyl lauroleate, 7%	
Hexadecenyl palmitoleate, 3%	
Oleyl physeterate, 3%	
Oleyl oleate, 15%	
Glycerides of Saturated Acids:	2%
Stearin	
Glycerides of Unsaturated Acids:	9%
Olein	
d-Glyceryl ethers of batyl, chimyl, and selachyl alcohols.	
Sterols:	0.4–0.5%
Cholesterol	

tilled the alcohols of sperm oil up to C_{18}, and reported the following: alcohols less than C_{14} 1 per cent, $C_{14}H_{29}OH$ 5–6 per cent, $C_{14}H_{27}OH$ 5 per cent, $C_{16}H_{33}OH$ 26–27 per cent, $C_{16}H_{31}OH$ 10 per cent, $C_{18}H_{37}OH$ 7–9 per cent, *cis*-$C_{18}H_{35}OH$ 17–19 per cent, *trans*-$C_{18}H_{35}OH$ 15–17 per cent and unsaturated C_{20} alcohols 10 per cent by volume. About 60 per cent of the alcohols are unsaturated.

Peculiarly, the unsaturated alcohol portion of the esters of sperm oil is as susceptible to hydrogenation as the unsaturated acyl part of the molecule; therefore the unsaturated alcohols are convertible to *myricyl*, *cetyl*, *stearyl*, and *eicosyl* alcohols, and the unsaturated acids to saturated acids. Hence hydrogenated sperm oil is capable of producing far higher yields of *spermaceti wax* of higher melting point and harder consistency.

Cholesterol is present in sperm oils to the extent of 0.44 per cent. Sperm and Arctic sperm (doegling) oils consist largely of esters of monohydric alcohols, but also contain small percentages of glyceryl ethers comprising *batyl*, *selachyl*, and *chimyl* alcohols.

Saturated and unsaturated wax alcohols of the unsaponifiable can be separated by the Grün-Janko bromine-ester method. Debromination of the ether-insoluble bromide is accomplished by treatment with zinc and glacial acetic acid, and the highly unsaturated alcohols (batyl, selachyl and chimyl alcohols) are liberated.

Toyama[276], and more recently Baer and Fischer[16], have studied the configuration of the glyceryl ethers. *Batyl alcohol* has been found to be identical with *d*-α-octadecyl glycerol, $C_{21}H_{44}O_3$ (m. 71°C). *Chimyl alcohol* is identical with *d*-α-hexadecyl glycerol, $C_{19}H_{40}O_3$ (m. 61°C). *Selachyl alcohol*, $C_{21}H_{42}O_3$ (liquid), according to Baer and Fischer[16], can also be assigned to the *d*- series, because it is reducible to batyl alcohol. It is found in the liquid portion of the unsaponifiable; the other two alcohols are solid, the chimyl predominating. The hydrogenated unsaponifiable matter melts at 64 to 68.5°C.

The glyceryl ethers were shown by André to occupy a position between the glycerides and waxes:

$(R\cdot CO\cdot O)_3\cdot C_3H_5$	$(RCO\cdot O_2)_2\cdot C_3H_5(OR')$	$R\cdot CO\cdot OR'$
glyceride	*glyceryl ether*	*wax*

Commercial Sperm Oil. The sperm oils have been graded by the oil refineries as (1) *winter sperm oil*, congealing below 38°F, the yield being about 75 per cent from the crude; (2) *spring sperm oil*, congealing at 50–60°F, 9 per cent yield; (3) *taut-pressed oil*, melting at 90–95°F, 5 per cent yield; and (4) *crude spermaceti*, melting at 110–115°F, 11 per cent yield. Sperm oil is a thin yellow liquid, and when of good quality is nearly free from odor. Allen gives its specific gravity ($d^{15.5}$) as ranging between 0.875 and 0.884; Ullman[288a] gives 0.877 and 0.885. Sperm oil stands at 44 to 46

on the Casartelli hydrometer. This hydrometer, used by dealers, shows water at 0 and rapeseed oil at 28. Southern whale oil is said to rate 24 on the same scale. The flash point must exceed 225°C. Ullmann gives the acid value of sperm oil as 0.1–0.3, saponification number 123–134, iodine number 68–85, and unsaponifiable 37–42 per cent.

Sperm oil, upon saponification, yields 39.2 per cent of wax alcohols and only 1.3 per cent of glycerol, and is therefore classed as a liquid wax. Cachalot yields 41.2–44.3 per cent, and Arctic sperm 38.0–39.2 per cent of wax alcohols. Sperm oil yields 60–63 per cent of insoluble fatty acids. Other oils (not liquid waxes) yield more fatty acids and 10–12 per cent of glycerol.

Sperm oil is preferable to any other fixed oil for lubricating the spindles of cotton and woolen mills, and delicate mechanisms like watches, because of its limpidity and freedom from tendency to "gum" and become rancid. It retains its viscosity at high temperatures. It is used to some extent as a burning oil in lamps, in hardening steel, in the manufacture of specialty soaps, in dressing leather, and as a drawing lubricant. *Bottlenose oil* and *Arctic sperm oil* are used for substantially the same purposes. Sperm oil is handled in drums and tanks as the source of cetyl alcohol.

When sperm oil is mixed with mineral lubricating oil (e.g., 1 to 10) and subjected to a silent electric discharge in a glass tube apparatus, there results a very pronounced increase in viscosity and consequently improved lubricating properties in engines. The polymerized liquid wax constituent of the sperm oil is soluble in the hydrocarbon oils; according to Russell[235], suitable formulations can be arrived at that will greatly increase the viscosities in the range of 540 to 2000 seconds Saybolt at 210°F.

Doegling or Bottlenose Oil

Doegling or bottlenose oil is a fluid very similar to sperm oil, particularly blubber sperm oil, with almost identical analytical constants. It can be distinguished from sperm oil by its taste. It is lower priced than sperm oil on account of its slight tendency to "gum." The constants for doegling oil have been given as: specific gravity (d^{15}) 0.875–0.890, acid number 0.1–0.4, saponification number 123–144, iodine number 81.3–84.0, unsaponifiable 32–41 per cent[268a].

Castor Oil Fish Oil

The castor oil fish, *Ruvettus pretiosus*, is a large deep-sea fish found in warm seas in the Atlantic and Mediterranean regions; its flesh contains an oil which is substantially a liquid wax. The fatty acids are combined with *cetyl*, *stearyl*, and *oleyl* alcohols, in proportions of 50, 6, and 44 per cent, respectively. The fatty acids comprise *oleic acid* (75 per cent), *hydroxyoleic*

acid (13 per cent), *stearic acid* (1–3 per cent), and monoethenoid C_{20} and C_{22} acids, as reported by Cox and Reid[61].

Whale Oils

The principal source of supply of marine oils is the whale. Whale oil, unlike sperm oil, contains little of the waxy constituents. In whaling today the blue whale is sought, as its yield of product equals that of the finbacks, two and a half humpbacks, or six sei-whales. These whales are all of the rorqual family, and differ from the sperm whales, bottlenosed whales, and dolphins. German whaling aims are concerned largely with the great blue whale, finback, and humpback, which provide food fats, specifically whale-oil margarine. Such fats are also of prime importance in the Scandinavian countries and elsewhere. American consumption of the oil, on the other hand, has thus far related chiefly to the manufacture of soap. High-grade tallows can be made by partial hydrogenation of whale oil, and complete hydrogenation results in a high-melting, more wax-like product. There are 24 floating factories and 281 whale-catchers operating in Antarctic waters, producing half a million tons of oil—a far greater output than that of the Arctic. The sperm whale is one of a family order largely confined to tropical waters, but stragglers reach both polar seas. Sperm oil is everywhere mixed with *spermaceti*, but most of the latter is obtained from the case occupying most of the snout of its enormous head, and yielding almost 500 gallons of mixed sperm oil and spermaceti. The production of sperm oil is insignificant in tonnage compared with that of common whale oil.

When the highly hydrogenated oil of the Antarctic finback whale is fractionally distilled it yields after hydrolysis the following proportions of carboxylic acids: C_{14} 6, C_{16} 34, C_{18} 30, C_{20} 19, C_{22} 5, and C_{24} acid 0.5 per cent[236a].

Ambergris

Ambergris is defined as a morbid secretion from the intestines of the sperm whale. Ambergris is usually found floating in tropical seas. It is a waxy material which is gray, yellow, white, or black in color. Pale-colored ambergris is so rare that it commands a very high price; its major use is as a fixative in fine quality perfumes. The Fisher-Johns melting point of a fine grade of white ambergris is 82.5°C, with a minimum (or softening point) of 52.5°C. Good samples of ambergris may have 55 to 95 per cent of ether-soluble material. It is also appreciably soluble in chloroform and in fats.

The chemical composition of ambergris is chiefly that of *coprosterol* (preferably called *coprostanol*, a dihydrocholesterol), $C_{27}H_{47}OH$ [m. 102–104°C, $[\alpha]_D$ + 24° in 13.7 % $CHCl_3$], and *epicoprosterol* (preferably called *epicoprostanol*), with a small percentage of *cholesterol* and *cetyl palmitate*

(m. 52.5°C). Hardwick and Laws[96a] state that ambergris is known to consist of *ambrein*, epicoprostanol, *arachidic acid*, *ambroporphyrines*, some ketones and a liquid paraffin. These investigators described a chromatographic separation of ambrein and epicoprostanol.

PART III: WAXES FROM PLANTS

The Ecology of the Plant Waxes

The outer wall of the epidermis of an adult plant leaf is thickened by the deposition of *cutin*, a fatty substance highly impermeable to water; usually the cutinized portion forms a continuous yellowish coat. Without cutin the thin epidermis would be permeable because of its cellulosic composition. In the grasses and the rushes, silica is deposited in the cell walls in addition to cutin. Plants of dry areas, such as deserts, dry rocks, and dry sands, are known as *xerophytes*, and their leaves are highly cutinized. Particularly is this true of the evergreen xerophytes, such as conifers, ericads (revolute type, i.e., with edges curved under), and some of the broad-leaved trees, e.g., live oak and olive. The leaves of many of the alpine and arctic plants and of the peat bogs are heavily cutinized; so also are those of the mesophytic evergreens (plants of fairly moist soil), such as the yew and the hemlock. It is believed that the heavy cutinization of the *mesophytes* of the dwarf plants like mountain hemlock (*Tsuga mertensiana* Carr.) may be due to limited root systems. Many leaves of these scraggy (Krumnholz) plants appear "glaucous," and have a bluish-gray film of wax, sometimes known as "bloom," which is removed by rubbing. Such waxy cutin retards the transpiration of water from leaves. Sometimes the wax deposits are thick, forming a brittle crust, as in certain fleshy perennial herbs like the succulent houseleek (*Sempervivum* spp.) and in the wax palms, or layers of vertical rods, as in sugar cane. De Bary[28] distinguished four characters of wax coating:

(1) Continuous layers of incrustations of wax, e.g., on the leaves and stems of common purslane, *Portulaca oleracea*; leaves of firechalice, *Zauschneria* spp; yew, *Taxus* spp.; the stems of the waxpalms, *Ceroxylon* spp., etc.

(2) Coatings composed of multitudes of minute rods placed vertically side by side upon the cuticle, e.g., on the stems of the sugar cane, *Coix lacrymajobi* L., and some other grasses.

(3) Coatings of minute rounded grains in a single layer, e.g., on the leaves of the wild cabbage, *Brassica oleracea botrytis*; onion, *Allium* spp.; tulip, *Tulipa* spp.; clove pink, *Dianthus caryophyllus* L., etc.

(4) Coatings of minute needles or grains irregularly covering the surface with several layers, e.g., on the leaves of the Tasmanian blue eucalyptus, *Eucalyptus globulus* Labill; rye, *Secale cereale*, etc.

As with hairs, but not with cutin, wax coats are best developed on the

underleaf surface where the stomata (pores) are the most abundant, as in this location it is the more effective in checking transpiration. Wax is not the only means, however, as nature provides resin, particularly where there is intense heat from the sun's rays, e.g., on the leaves of the creosote bush, *Larrea tridentata* (*Covillea tridentata* Vail.), and on many other desert xerophytes.

Wax may form an incrustation over the whole leaf, as in the bog bilberry, *Vaccinium uliginosum* L., which grows on the summits of mountains in New England and in the Adirondacks; or only on the stomatiferous lower face, as in the bogrosemary, *Andromeda polifolia* L., an evergreen shrub; the small cranberry, *Vaccinium oxycoccus* L., a creeping evergreen vine; the birdseye primrose, *Primula farinosa* L., a species of willow, *Salix groenlandica*; and the carnation sedge, *Carex panicea* L. Wax is excreted over the surface of certain *hydrophytes* to protect them from saltiness, as in the North American swamp-plants, *Acer rubrum* L., red or swamp maple, and *Persea pubescens* Sarg., swampbay persea, and others.

The degree to which wax on cuticle surfaces of the leaves, stems and fruits depresses transpiration was experimentally established by Tschirch and Haberlandt[109] in 1882. Usually the coating produced is only a thin one, but to take an opposite case, the common caper, or hyssop of the Scripture, *Capparis spinosa* L., at the commencement of the dry season in the Egyptian desert, excretes a very thick layer of wax over the whole leaf surface that completely prevents transpiration. The thickness of the heavier wax coatings may range from 1 mm as in *Sarcocalla* spp. in South Africa to 5 mm in *Ceroxylon* spp. in South America. Bloom-covered leaves usually have no sharp teeth at their margins, and possess at most rounded teeth provided with hydathodes. As wax prevents water from wetting leaves, it protects ombrophilous foliage from rain.

A group of xerophytic plants known as *halophytes*, since they are associated with salt water in maritime areas, have a glaucous, or mat blue-green surface, on their leaves due to the wax coating, e.g., the seapea, *Lathyrus maritimus* L.; the seaholly eryngo, *Eryngium maritimum* L.; the sea bluebells, *Mertensia maritima* L.; yellow hornpoppy, *Glaucium flavum* Crantz; and the common colewort *Crambe maritima*. Included in these dune plants is European dune wildrye, *Elymus arenarius*, which has broad leaves glaucous with wax, like those of the *Triticum junceum*, also of grass genera.

In the fruits, deposits of wax in the cutinized layers of the epidermis cause water to flow over the cuticle without being absorbed. This is the case in such fruits as plums and grapes, on which the wax covering forms the so-called bloom; it may consist of grains, small rods, or crusts.

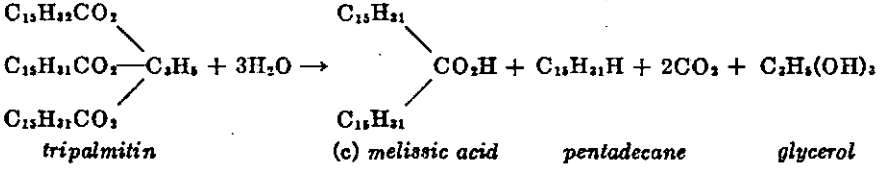
Formation of Wax in Arid Plants. The plants which produce the greatest amount of wax for their weight are those found in hot or tropical climates, particularly in arid regions. Waxes from such plants have an

appreciable amount of hydrocarbons in their chemical composition; for example, candelilla wax contains nearly 50 per cent. Some plants in the temperate zones produce waxy material in their fruits, but this is of a fatty nature, largely if not wholly consisting of one or more triglycerides, for example, the wax of the myrtle berry.

In the arid plants, glycerides in the form of fat or oil, built up by a reductive process and carboxylation, apparently are transformed into new chemical entities, such as high molecular weight alcohols, acids, and hydrocarbons. These processes are the result of the metabolic changes occurring daily according to the presence or absence of light action, warmth, and moisture, and the nature of the plant species. The processes of nature involve carboxylation, reduction, hydrolysis, oxidation, decarboxylation, and the photochemical reaction between hydrocarbons and hydroxy acids to form esters containing an even number of carbon atoms, and water.

For example, if *tripalmitin* and *palmityl alcohol* are taken as representative constituents of the fat, or oil, found in the pollen or tissues of plants, we might expect to obtain *melissic acid*, *pentadecane* and glycerol by hydrolysis and decarboxylation of this glyceride. When sunlight is absent, the glycerol so formed would tend to retain moisture, but the arid condition of the soil probably withdraws the glycerin to the plant roots, and hastens the formation of more wax acids and hydrocarbons in the exposed portions of the plant, thus reducing oily or fatty constituents to a minimum.

The decarboxylation of natural vegetable fats and oils proceeds in stages. With *tripalmitin* it probably proceeds to a secondary stage with the elimination of just two carboxyl groups, as shown in the reaction:



tripalmitin (c) *melissic acid* *pentadecane* *glycerol*

Cetyl alcohol, which accompanies the glyceride, would assimilate the nascent CO_2 to produce *hydroxymargaric acid* thus:

$$C_{15}H_{31}\cdot OH + CO_2 \rightarrow C_{15}H_{30}O\cdot CO_2H$$

cetyl alcohol *hydroxymargaric acid*

Pentadecane arising from the decarboxylation then reacts photochemically with the hydroxy acid to produce *cetyl palmitate*, which on subsequent decarboxylation yields *hentriacontane*,

$$C_{15}H_{31}H + HO\cdot CO_2\cdot C_{15}H_{33} \rightarrow C_{15}H_{31}\cdot CO_2\cdot C_{16}H_{33} + H_2O$$

pentadecane *hydroxymargaric acid* *cetyl palmitate*

$$C_{15}H_{31}CO_2\cdot C_{16}H_{33} - CO_2 \rightarrow C_{31}H_{64}\cdot H$$

cetyl palmitate *hentriacontane*

WAXES FROM PLANT LEAVES AND STEMS

Classification

Waxes from the leaves and stems of plants may be grouped in the following manner for the sake of convenience.

(1) **Waxes of palms.** The palm family, known as the Palmae (Palmaceae), is of great economic value. The wax is generally more abundant on the leaves than on other parts of the plant. The wax-bearing palms, include *Copernicia cerifera*, the source of carnauba wax, *Attalea excelsa*, *Ceroxylon andicola*, *Raphia pedunculata*, etc.

(2) **Waxes of shrubs and herbs.** Wax-bearing shrubs include *Pedilanthus pavonis*, the source of candelilla wax; *Euphorbia stenoclada*; *Ceanothus velutinus*; *Gossypium arboreum*; *Musa textilis*; *Spartium junceum*; *Thea sinensis*; etc. The wax is often distributed over all parts of the shrub above the soil, whereas the wax on an herb is minute in quantity and usually confined to the leaf. Such herbs include species of *Brassica*, *Allium*, *Tulipa*, *Dianthus*, *Ergium*, *Linum*, *Mertensia*, *Glaucium*, *etc.*, scattered over many families. They also include parasitic perennial herbs such as *Balanophora*, and leaf wax-bearing perennials such as *Calathea lutea*.

Waxes of succulent plants. There are a great number of succulent (juice or flesh bearing) plants which contain waxes. The succulents which bear waxes are of the following genera: *Agave*, *Euphorbia*, *Fouquieria*, *Furcraea*, *Pedilanthus*, *Sempervivum*.

The sisal hemp, *Agave sisalana*, contains an appreciable amount of wax, as does henequen, *Agave fourcroydes*. The waxes are classified with those of other fibers (see p. 208). The most important wax-bearing plant of the Euphorbia is candelilla, *E. antisyphilitica* (see p. 184). Flat-stem Euphorbia, *E. xylophylloides*, and other species are described under Madagascar waxes (see p. 216). Since the bark of the succulent ocotillo, *Fouquieria splendens*, yields wax, the wax has been classified under waxes from barks (see p. 263).

A succulent known as piteira furcrea, *Furcraea gigantea*, yields a wax not unlike hemp wax (see p. 207). The wax of the slipperflower, *Pedilanthus aphyllus*, and that of the waxslipperflower, *P. pavonis*, are associated with candelilla (see Candelilla wax, p. 184). The houseleek, *Sempervivum acuminatum* Schott, contains a minute amount of wax.

(3) **Waxes of grasses and sedges.** This group comprises the plant order Graminales, which has two families, the grasses (Gramineae) and the sedges (Cypernaceae). The Gramineae rank close to the Palmae in their economic value in wax production. The Cypernaceae have only a minute proportion of wax and are of little or no economic value otherwise. The *Gramineae* include forage grasses, cereal grains, and other plants of economic value that contain an appreciable percentage of wax. The forage grasses

include *Dactylis glomerata, Lolium perenne, Medicago sativa,* etc., which contain small concentrations of wax. The cereal grains include *Triticum aestivum, Oryza sativa,* etc. Grasses not classed as of forage or cereal value, include species which yield waxes worthy of economic recovery, such as *Stipa tenacissima,* the source of esparto wax, *Lygeum spartum, Sasa paniculata, Coix lacrymajobi, Sorghum vulgare, Glyceria ramigera,* etc.

Waxes of canes. The canes include the tribe of Calameae of the palm family, order Palmaceae. *Calamus rotang* L. and several other species include the rattan or cane palms of India and the Malayan Islands. These slender reed-like stems contain little or no wax. The sugarcane, *Saccharum officinarum* L., of the grass family, order Gramineae, has an appreciable deposit of wax on the surface of the stalks. This wax is of considerable economic value when recovered.

(4) **Waxes of broad-leaf trees.** The broad leaves contain only minute percentages of wax, e.g., *Eucalyptus globulus,* the wax of which may be recovered from its essential oil, *Theobroma cacao, Santalum album,* etc. The broad leaves of maple, beech, and oak when mature contain waxes which have *cerotic acid* and *phytosterols* as constituents.

(5) **Waxes of narrow-leaf trees.** The narrow leaves, or needles, are characteristic of conifers. The wax is recoverable in small quantity from the distillate of the essential oil of the conifer. The conifers which have been investigated for waxy constituents include *Juniperus sabina, Picea excelsa, Pinus sylvestris, Thuja occidentalis,* etc.

(1) Waxes of Palms

The palm family, Palmae, of the order of Spadiciflorae, comprises a number of tribes of palms, several of which are wax-bearing. The tribes of the Palmae are:

I. *Cocoineæ,* which includes *Elaëis guineënsis,* the West African oil-palm; *Attalea funifera,* which furnishes piassava fiber and a seed oil; *Attalea excelsa,* the source of ouricury wax (see p. 178); and *Cocos coronata,* from which licuri wax is derived (see p. 179).

II. *Coryphineæ,* which includes *Copernicia australis,* the source of caranday wax (see p. 173); and *Astrocaryum murumurú,* the wax-bearing seed of which furnishes a vegetable tallow (see p. 294).

III. *Sabaleæ,* which includes many species of fan palms, such as *Sabal palmetto* Walt., that spread from Venezuela to the West Indies. Tribe II is sometimes classified under Tribe III.

IV. *Borassinæ,* or *Borasseæ,* which includes fan palms of such genera as *Hyphaene, Lodoicea,* and *Borassus.* The Doum palm, *H. thebaica,* has a tall aerial stem and branching leaves. *B. flabellifera* furnishes sap which yields a palm wine, and an ornamental wood, called palmyra wood. The *H. schatan* Boj. contains wax in the stem, petiole, and lamina.

V. *Arecineæ*, which includes *Ceroxylon quidiuense* Karst. Wendl., and *Ceroxylon ferrugineum* André, the leaf stems of both of which are coated with a resinous wax (see p. 176). Arecineæ is the largest tribe, and includes *Caryota*, *Arenga*, *Oreodoxa* (Royal palm), and a number of other genera.

VI. *Lepidocareæ*, which includes *Raphia pedunculata*, the source of raffia wax (see p. 183); Rattans (Calamaea); the sago palm, *Metroxylon* spp., which has a starchy pith that is highly valued; the mauritia fan palm; and others.

VII. *Phoeniceæ*, which comprises the single genus *Phoenix*. *P. dactylifera* is the cultivated data palm, and yields a minute amount of wax[148].

VIII. *Phytelephanteæ*, which includes *Phytelephas macrocarps*, the source of vegetable ivory, and *Nipa fruticans*, a tropical Asiatic fossil palm. The tribe is not wax-bearing.

Carnauba Wax

Carnauba wax is obtained from the leaves of a species of an American genus of palm designated as *Copernicia cerifera* Martius, named in honor of Copernicus. The name *carnauba* is believed to be a corruption of the Tupi *carnahyba*, compounded from *caraná* or *carandá*, meaning scaly, thick-skinned, or thick-barked, and *yba*, meaning tree or palm.

C. cerifera grows in the dry desolate country in the region of Ceará, northeastern Brazil. It grows in lesser quantities in the south of Brazil and the Chaco country in northern Argentina and Paraguay. The wax-gathering industry is centered in Parahyba moving northward to Rio Grande do Norte, and Ceará, but also extends eastward to Piauhy (Piauí) and the state of Maranhao. The largest export center is Bahia on the Atlantic Seaboard. The first large shipments of the wax were made from Ceará in 1845. In Europe the wax has been an article of trade for more than a century. About two-thirds of the product now comes into the United States.

The carnaúba is a straight-trunked palm of slow growth, attaining an average height of 25 to 35 feet, but seldom more than 40 to 50 feet even after 50 years of growth. The bark is scaly, rough, and thick, and the leaves grow out from yard-long petioles in wide serried fan shapes. The tree reproduces prolifically. The ovaloid fruit resembles a hazel nut, and when ripe it falls to the ground, where dense clumps of shoots spring up, some of which survive to form saplings.

The flowers are monoecious, very small and numerous, and grow from an appendix in the axils of the leaves. During the dry months the leaves and petioles exude a wax through the pores. Nature provides this wax to prevent excessive evaporation of water from the plant. The summer sun from July to December seems to stimulate the production of wax, although

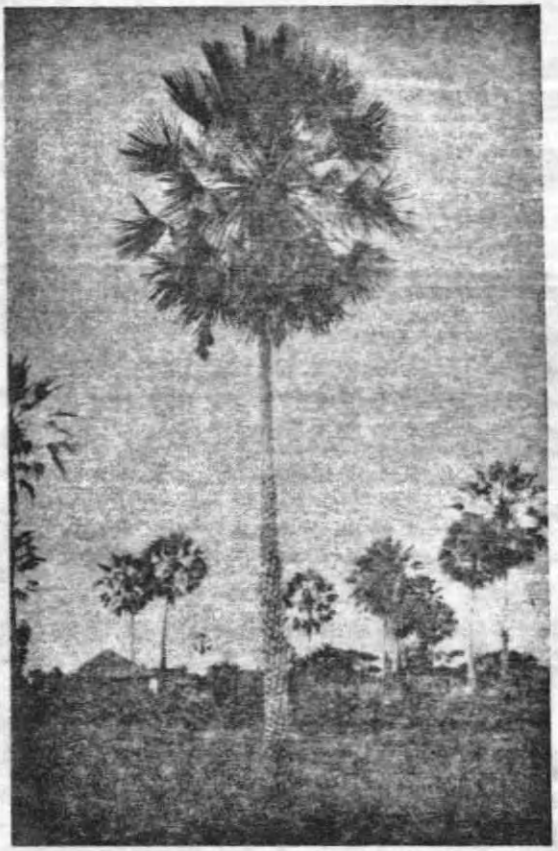


FIGURE 4. *Copernicia cerifera* Mart. Well developed carnauba palms on dry ground which is only subject to periodic floods. Parnahyba, Brazil.

the available wax may even increase with the occasional winter rains. The best quality of wax is obtainable from the young tender leaves which are gathered three times from September to March.

There are two varieties of the carnauba palm south of the banks of the São Francisco River, which the natives distinguish as white and red. A black variety also exists. The palms have no master root; the roots stretch out over the surface of the ground in search of moisture. The carnauba palm prefers to grow along the banks of rivers and lakes, but it is also found in small isolated groves from the damp lowlands along the coast to the forests of the interior.

Economic Value of the Carnauba Palm. The carnauba palm is of great value to the *sertanejos*[307], the inhabitants of these flat semiarid lands, and the historical evolution of the Brazilian *setao* is closely allied with this

FIGURE 5. A grove of carnauba palms along the river bed of the Parahyba, Brazil. The carnauba palm prefers to grow along the banks of rivers and lakes.

rough-barked, fan-topped palm, which supplies him not only food, drink, and a cash crop, but also fibers for clothing, timber for housebuilding, and even his light. The timber is hard and useful for laths to take plaster, pilings which will resist the brackish waters, bridges, fences, and excellent furniture. It is almost impervious to the attack of insects. The bark may be used as firewood. The leaves are utilized for window and door shades. There is food value in the tender end shoots and from them can also be made wine, vinegar, and a saccharine substance. The bunches of fruit, rust-colored when ripe and dried, may be crushed for cooking oil. The roasted and pulverized fruit may be brewed to a coffee-like drink. A starchy flour like manioc flour can be prepared from the medullary pith, or the pith may be fermented to an alcoholic drink. A medicinal is extracted from the roots. The saplings and tender shoots are fed to cattle in case of drought.

The important hat industry of Ceará uses the superior quality of carnauba leaves, turning them into hats similar to Panamas which are shipped

everywhere in Brazil. The natives sleep in hammocks made from the fibers. Fine cordage, nets, baskets, mats, and curtains are also woven from the fibers. The fiber from the petiole is made into brooms and brushes. Although only the wax has given the carnauba palm universal renown, it can be readily understood that there is no plant in existence that is of greater value to the Brazilian native. For light he melts a small portion of tallow with the wax, and solidifies the melt around a cotton wick to form a candle. The carnauba candle, however, is not the best source of illumination!

Harvesting the Carnauba Leaves. The cutting of the leaves and sprouts generally takes place during the dry months of the year, usually between September and December or January. The production of carnauba wax has been described by Walmsley[307]. Workers known as *moradores*, a class of herdsmen, contract with, or are hired by, the proprietor to remove the wax from the leaves of the stand of palm trees, and to melt it for shipment. The *moradores* are also sometimes squatters on the property, and receive a share in the profits of the harvest on the share-cropping principle. They chop through the stems with a *foice*, a curved sickle-like knife fastened to the end of a long pole. As the leaves fall to the ground the long stems are slashed off and then the leaves are carefully transported to a central terrace for drying in the sun. There are two cuttings (sixty days apart) per tree in a normal year, but there is a yield of only eight to twelve leaves per cutting. Only mature leaves are harvested. The sun-drying takes from three to five days. A suitable drying terrace consists of a tiled or cement floor 10 to 14 feet square surrounded by an unroofed wall 2½ feet high. The wax dust is very light and flour-like and is easily dispersed by a slight gust of wind.

From the drying terraces the leaves, with their wax loosened by sun-drying, must be transported with the greatest of care to the shed for trenching, threshing, and beating. The shed is about 15 feet long and 12 feet wide, and so constructed as to prevent any gust of air from passing through it. The operators work with the door closed, and trench leaves over tooth-like blades fixed upright in a block of wood. The idea is to cut through the fiber, thus splitting the wax-containing ribs apart and opening up the webs. The leaf is then ripped apart by hand to loosen the wax, and the leaves in small bunches are beaten against a sort of wooden sawhorse to remove all the wax dust. The spent leaves are thrown out of the hut. Afterwards the dust is swept into small bins or closely woven bags preparatory to melting. The walls and roof are also brushed to remove wax powder. Three workers can handle about 4000 leaves a day.

Preparation of Carnauba Wax. The procedure of harvesting and the recovery of the powdered wax is commonly followed in the State of Ceará.

In Piauhy, which is the only other very large producing state, the practice is a little different, because of the danger of expected rain. The green leaves are slit by long sharp knives into fine shreds which remain attached to the butt end of the leaf, and the leaves are sun-dried for only one day.

Wax in the powdered form is often bagged and shipped to the coast for melting and refining, but the common practice is to melt it at the plantation. Melting is carried out in the so-called melting room in either clay vessels or open iron pots, directly over a wood or charcoal fire. In the native processing of carnauba wax, the flour is sometimes melted down in an old 5-gallon petrol can from which the top has been removed. A full 5-gallon can of powder will melt down to less than a quart of molten wax. The wax is slowly melted over a fire, being stirred constantly during the operation, and then strained through a thick cloth.

Various modifications in the recovery and melting procedure are essential to obtain the classified grades of carnauba wax, as they are known commercially. A brief description of these grades will be given. About 30 per cent of the total production is the melt from the *olho* leaf—the young, yellow, unopened leaf that grows upward from the "cabbage ball," at the center of the palm. The powder is melted and the "top portion" drained into little pans or saucers. Occasionally the wax may show an embossing mark of the container after its removal. This wax is known as *cera flor* or *flor fina*. It represents only one per cent of the total production of carnauba wax and is the most expensive. In straining the bulk of the molten wax of the "olho" leaf through cheesecloth, *primiera* or *amarella primiera* (Yellow No. 1) is formed, which has a somewhat murky, pale yellow color, compared to the clean and more straw-like color of *flor fina*. *Mediana clara* (Yellow No. 2) is quite similar, but grayish in color. Inferior grades are *mediana roxa* and *cauhype*, which represent the wax recovered from the residues, and are consumed locally for the most part. They are gray and grayish-black in color.

Approximately 70 per cent of the output is obtained from the *palha* grades, which are produced from the *palha* leaf, i.e., the fan-spread leaf harvested from the same tree as the *olho* leaf. These *palha* waxes are more greenish in color, varying from a pale greenish-yellow, characteristic of the large mature leaves, to a pale gray-green; the inferior grades are gray, dark gray, or even black. The *palha* wax termed *gordurosa*, meaning waxy, is known in the foreign market as "North Country wax." In its preparation the melted wax is drained into petrol cans, after straining through cotton or burlap, and through beaten fibers or leaves. If the chalky grade known as *arenosa*, meaning chalky, is desired, it is made by adding a cup of sour salt water to the *palha* wax while melting it. *Arenosa* is a more friable, porous wax of a pale grayish-green color produced at the will of the native worker.

Instead of filtering the wax as above described, the molten wax is sometimes quickly poured through a cheesecloth held by two natives for the filtration, and then the center mass is squeezed with a pair of large wooden pincers to get the wax out of the residue. Some of the less primitive establishments use a crude type of wooden filter press. The cheesecloth holding the molten wax is placed in a cavity in a log over the bottom of which strong fibers have been stretched. A block is placed on top of the folded cheesecloth, and a long heavy pole is used as a lever to express the wax from the cake. The molten wax is caught in an earthenware pan of about 3 kg capacity and allowed to cool; the hardened wax is broken away and hammered into chunks, and the residue is recovered later.

A limited amount of carnauba wax has been commercially produced in Brazil by solvent extraction of wax from the plant cuticle. In general the solvent extracted wax is more resinous, not as readily compatible with other waxes, and generally inferior to the concentrated wax recovered by the mechanical process described. Solvent refining of the concentrated wax is sometimes resorted to and is less costly than solvent extraction of the whole plant. Steinle[259a] says that where solvent extraction is necessary and economically feasible, the process should be carefully designed to yield a wax having optimum desirable characteristics, since solvent extraction can often make or break a given plant wax.

Yield of Wax. The yield of wax per leaf varies with the age of the tree, the locality, and the amount of rainfall which preceded the harvest. On an average a leaf will yield about 5 grams of wax. With a maximum cutting of twenty leaves per year from a free, five carnauba palms will produce above one pound of wax a year. The measure for carnauba wax is the *arroba*, equivalent to 33 pounds. About 15,000 to 30,000 *palhas*, or 28,000 *olhos*, are required to make one *arroba*. The average yield of the wax for each tree is only 2.8 ounces per cutting. There are probably 50,000,000 trees in production, and of these 20,000,000 are estimated to be in Ceará and Piauí, and 5,000,000 to 6,000,000 in Rio Grande do Norte.

Properties of Carnauba Wax. Carnauba wax stands out preëminently as the best of the polishing waxes. It combines hardness with toughness, wear resistance, and lustre of its films. It is compatible to a high degree with other waxes. It is sparingly soluble in organic solvents in the cold, but quite soluble hot; the solution on cooling deposits the wax which in turn retains the solvent well, thus preventing excessive solvent losses by evaporation at ordinary room temperature. Table 35 gives the solubility of carnauba wax in various solvents at a temperature range of 25 to 30°C.

At 45°C, 3 g of carnauba wax dissolve in 100 g of V.M. & P. naphtha (sp. gr. 0.750 at 15.6/15.6°C; 7 g in 100 g of solvenol (terpene hydrocarbons); and 11 g in 100 g of turpentine (sp. gr. 0.860).

TABLE 35. SOLUBILITY OF CARNAUBA WAX IN VARIOUS SOLVENTS, 25–30°C

Solvent	Solubility: Grams per 100 ml Solvent	Solubility: Grams per 100 Grams solvent
Ethyl ether	0.421	0.594
Methanol	0.179	0.226
Ethanol (95%)	0.141	0.174
Benzene	0.518	0.590
Chloroform	1.690	1.145
Acetone	0.323	0.410
Xylene	0.610	0.709
Ethyl acetate	0.374	0.412
Turpentine, gum	0.440	0.508
Naphtha, high b.p.	0.219	0.281

At 50°C, 20 g of carnauba wax dissolve in 100 g of V.M. & P. naphtha; 11 g in 100 g of solvenol; and 21 g in 100 g turpentine.

Characteristics of the Grades of Carnauba Wax. The grades of carnauba wax are as follows:

Provincial Name	Commercial Designation
Flor fina	Yellow No. 1
Primeira	Yellow No. 2
Cauhype	Cauhypa
Mediana clara	North Country No. 2
Gordurosa	North Country No. 3
Mediana roxa	Fatty Gray
Arenosa	Chalky

It would appear that the highest wax content (99.32–96.65 per cent) and the highest iodine numbers (10.8–12.1) are given by grades *flor*, *primeira*, and *clara*, although they are the lowest in melting point (83.5–84.9°C)[85a]. A lower wax content (96.91 and 97.16 per cent) is given by grades *gordurosa*, *mediana roxa*, and *arenosa*; they also have lower iodine numbers (8.0–9.9) and higher melting points (85–86°C. *Mediana roxa* has an iodine number of 9.87[43]. A study made by Marsel[179a] in 1950 of carnauba wax covered 56 samples having commercial designations as listed above. These samples were received expressly for a project sponsored by the American Wax Importers and Refiners Association, Inc., New York.

Marsel[179a] reported on the dirt, saponification values, acid numbers, melting points, iodine numbers, flash points and emulsification characteristics of four groups of carnauba wax. The first group (I) covered #1 Yellow and #2 Yellow, prime waxes obtained by cutting the smaller and less mature leaf. The second group (II) covered Cauhypa and North Country #2, of which Cauhypa has the better color. The third (III)covered Fatty Gray and North Country #3. This represents wax obtained by cutting the mature leaf and is much darker in color than the Yellow. The fourth group

TABLE 36. ANALYTICAL CONSTANTS FOR CARNAUBA WAX

Specific Gravity	
at 15°C	1.0008[k], 0.990–0.999[a], 0.995–0.999[b], 0.999[n]
25	0.9988[k]
38	0.9950[k]
44	0.9930[k]
90	0.8484[k], 0.850[a]
94	0.8455[a]
98	0.8430[k], 0.8420[a], 0.8422[n]
100	0.8415[k]
Melting point (°C)	84[c], 78–85[d], 83.5[b], 83.3[e], 83[f], 85[l], 80–84[m]
Capillary	84[h]
Ring and Ball	85[f]
Ubbelohde	83[f]
Setting point (°C)	82[f]
Softening point (°C)	81.1[a], 82[f]
Liquating point (°C)	80.6[f]
Acid value	2.9[h], 4.0[g], 4.2–5.4[b], 5.0[i], 9.7[j], 7.9[k], 7.2[m], 3.9[q]
Saponification number	88.3[h], 87–84[a], 79–95[l], 78[m], 79–82[b], 81.9[q] 81.6[o]
Iodine number	13.1[h], 9–13[a], 7–14[d], 7.2–9.2[b], 9.9[m], 13.5[n]
Refractive index	
at 40° C	1.4672–1.4720[p]
60	1.463[p]
90	1.4496[p]
100	1.4457–1.4478[p]
Acetyl value	54.8–55.2[a], 39.4 ± 5.4[m], 50.5[q]

[a]Lewkowitsch;[b]Farcy[178]; [c]Wiesner; [d]Sweet; [e]Bulatkin for No. 1 carnauba; [f]Rainer; [g]Hübl; [h]Radcliffe; [i]Allen; [j]Eichhorn; [k]Warth; [l]Gomez; [m]Bunger and Kummerow (1948) for fatty gray; [n]Anon.; [o]by Hezel method; [p]Marsel *et al.* (1952)[178b]; [q]Findley and Brown (1953).

(IV) covered Chalky wax, which is obtained by adding a little water (5–10 per cent) to the wax during the melting process. The properties of these groups are as follows:

	Group I	Group II	Group III	Group IV
Sapon. number	70–83	75–79	73–84	70–76
Acid value	1.0–2.0	1.5–4.0	2.5–5.0	3.5–4.5
Melting point	82.8–84.4°C	83.6–84.8°C	83.2–86.0°C	84.0–85.2°C
Flash point	520–620°F	580–610°F	520–600°F	580–610°F
Iodine number (Hanus)	9.5–10.6	9.4–10.4	8.8–10.7	8.5–10.2

Dirt values from all samples ranged from negligible to 6.5 per cent. The yellow waxes were most free from dirt, containing up to 1 per cent. Acid values of yellow waxes are much lower than darker waxes. Marsel[179a] reports that a hot solvent mixture of isopropyl alcohol, *n*-amyl alcohol, and toluene will give a sharp indicator end point, with the use of phenolphthalein indicator and methylene blue as the masking agent, thus neutralising color effects of the wax. Precision of the method is ±0.2 for acid

value and ±1.5 for saponification number. Determinations are said to check well with titrations made with a Beckman pH meter. As a whole it was found that better emulsions are obtained with waxes having a flash point below 570°F.

Two specimens of Refined North Country #2 carnauba wax melted at 83.6 and 83.4°C, and showed a penetration (100 g/5 sec/25°C) value of $0.9^{3/2}$. When heated in an open cup the specimens starting smoking at 190°C, smoking badly at 270° and 265°C respectively. They flashed at 290° and 293°C (554° and 559°F), and boiled at 320° and 315°C. The fire points were 334° and 327°C respectively.

Melting Points. The Ball and Ring melting point is a trifle higher than the dropping point (ASTM). Fisher-Johns melting points may be recorded as *minimum*, which is the first indication of softening, and *maximum* when the pin point specimen has entirely melted. The F-J minimum is a degree or two lower than the softening point (S.P.) of the wax under water.

Penetration Values. The penetration values for No. 1 Yellow carnauba wax ranged from 0.9 to 2.4, averaging 1.25 for 100 g/5 sec/25°C readings. Penetration values for #2 North Country were 1.1 to 1.3, averaging 1.2; for #3 North Country 1.0 to 2.8, averaging 1.6. The durometer readings were 100 at both 0 and 25 on the 12 specimens of No. 1 Yellow tested. A spurious No. 1 Yellow gave a penetrometer reading of 1.1. A refined flake carnauba wax had a melting point of 180°F (ASTM), 178° F (F-J); a softening point (CC & S) of 176°F; and a penetration value of 2.0.

Refractive Index. Marsel and associates[179b] give the refractive index (n_D^{100}) of pure carnauba wax as 1.4478 (max.), and of refined prime candelilla as 1.4520. Pure No. 3 North Country carnauba has a refractive index (n_D^{100}) of 1.4472. Resins, both natural and synthetic, have a refractive index of 1.508–1.532; 5 per cent of such resins (e.g., Durez #219, n_D^{100}) will raise the refractive index of carnauba slightly above 1.4500. A rough estimation of the amount of resin present as an additive to the carnauba may be made by determining the refractive index of the specimen at 100°C. These investigators established a mean value of 1.4469 for the refractive index

TABLE 37. MELTING POINTS (°F) OF AVERAGE SAMPLE OF SHIPMENTS

Grade	Number of Samples	M.P. ASTM	M.P. B&R	S.P. CC&S	M.P.—Fisher-Johns Max.	Min.
No. 1 Yellow	16	183.2	183.6	179.8	182.9	177.8
No. 2 Yellow	1	182.0	—	180.0	—	—
No. 2 North Country	3	183.8	185.3	179.5	185.9	178.7
No. 3 North Country	3	182.9	183.5	179.0	182.3	176.9
Spurious No. 1 Yellow*	1	160.9	160.9	158.0	159.8	149.9

* When the specimen was heated highly it developed a deep orange color and the odor was strongly tallow-like.

(n_D^{100}) of carnauba wax, based on their tests of 19 samples of known purity. A variation in refractive index of from 1.4457 to 1.4478 was obtained on samples tested which comprised crude, refined, and bleached carnauba, and included all of the commercial grades by which the wax is commonly designated.

The refractive index at 40°C by the Zeiss butyro-refractometer of carnauba wax was recorded by Lewkowitsch as 65.7–69.0°. Carnauba wax is the only wax known that has a pronounced electrostatic property, and is similar to amber in this respect. The electrostatic property is particularly noticeable when the wax is finely ground.

Aniline Point. Carnauba wax has an aniline point of 78. To determine the aniline point the melted specimen of wax is neutralized with NaOH (15 per cent at 60°C) and mixed with the same volume of benzin. Five per cent of the mixture is placed in an apparatus and 5 ml of aniline added to determine the "aniline point." The following values for the aniline points of various waxes have been reported: beeswax 62–65, japanwax 36–37, white wax (beeswax) 61, and paraffin 115–117.

Chemical Constitution of Carnauba Wax. Carnauba wax contains straight-chain alcohols of even carbon number from C_{24} to C_{34}, the higher alcohols predominating, as noted by H. Stürcke[265a] in 1884, and confirmed by Koonce and Brown[139] in 1944. The latter investigators isolated *octacosanol* (C_{28}), *triacontanol* (C_{30}), and *dotriacontanol* (C_{32}) by fractional distillation using a helix-packed column at a pressure of 0.28 to 1 mm; they reported the C_{32} alcohol as the principal constituent of the unsaponifiable. The presence of a considerable amount of a C_{30} alcohol (m. 85.5°C) in carnauba wax appears to have been first noted by Stürcke.

Murray and Schoenfeld[195] recently investigated the composition of the nonsaponifiable portion of carnauba wax, using a modified spinning band column which proved very suitable for the fractionation of high-boiling material. The recovered alcohols from the nonsaponifiable portion of 200 grams of carnauba wax (Flor fina Yellow No. 1) were pale yellow, melted from 84.8 to 85.5°C, and weighed 107 grams, or 53.5 per cent of the wax. The alcohols were then acetylated and distilled at 0.5 mm pressure. The recovered C_{32} alcohol crystallized from petrolic ether in large laminae, which melted at 89.3 to 89.5°C, and resolidified at 88.9°C (acetate 72.4–72.5°C). The other alcohols recovered were C_{24} (m. 74.3–74.6°C), C_{28} (m. 82.8–83.0°C), C_{30} (m. 85.4–85.6°C), and C_{34} (m. 91.4–91.9°C). The earlier literature refers to the presence of a C_{27} alcohol (m. 80–82.5°C) named *carboceryl alcohol.* Carboceryl alcohol may be a dimeric mixture of C_{26} and C_{28} alcohols, both of which are known constituents of the wax.

The straight-chain alcohols were estimated by Murray and Schoenfeld to comprise: below C_{24}, 1 per cent; C_{24} to C_{26}, 4 per cent; C_{28}, 5 per cent; C_{30},

14 per cent; C_{32}, 51 per cent, and C_{34}, 22 per cent. In addition, three high-melting alcohols, totaling 2 per cent of the wax alcohols, have been isolated and appear to be closely related glycols. Stürcke[265a] in 1884 had reported isolating a glycol (m. 103.5–103.8°C) to which he attributed the formula $C_{23}H_{46}(CH_2OH)_2$. Stürcke had reported his C_{25} glycol (ω-diol) as convertible to the corresponding dibasic acid, $HOOC \cdot CH(CH_2)_{21} \cdot COOH$ (m. 102.5°C), known as carnaubandioic acid.

Murray and Schoenfeld[195] in 1951 isolated three diols (C_{22}, C_{24}, C_{26}), and recently [*Australian J. Chem.*, **8**, 432–426 (1955)] isolated an additional one (C_{28}). At the same time they indicate that a substantial amount of still higher diols are present in carnauba wax. The principal diol isolated, $HO(CH_2)_{24}OH$, was found to be identical to one they prepared synthetically. The diols comprise 6–7 per cent of the alcohols of carnauba wax (Flores No. 1), and the proportions of each diol were as follows: below 22, 3%; C_{22} 12%; C_{24} 23%; C_{26} 9%; C_{28} 14%; above C_{28} 39%. The melting points for the diols were as follows: *1,22-docosanediol* 105.6–105.7°; *1,24-tetracosanediol* 108.4–108.6°; *1,26-hexacosanediol* 110.4–110.5°; *1,28-octacosanediol* 112.2–112.3°; and undistilled diols 109–109.6°C.

Leys[160], at the Municipal Laboratory in Paris, had reported in 1913 that carnauba wax contained 49.2 per cent of alcohols. The nonsaponifiable was determined to be 54.7 per cent by Allen and Thomson, and the total alcohols as 52.4 per cent by Ashbutt. Bunger and Kummerow[43] reported the presence of 54 per cent of alcohols in a fatty gray carnauba wax having a saponification number of 78, and an acetyl value of 39.4 ± 5.4. Murray and Schoenfeld[195] saponified 200 grams of cleaned wax by boiling with alcoholic KOH (50 g in 1 liter 97 per cent alcohol) and 500 ml of petrolic ether (b.p. 80–100°C) for 24 hours. Water (600 ml) was then added and the petrolic ether layer separated while hot. The recovered alcohols, as previously stated, amounted to 53.5 per cent of the wax. According to Leys[160] the wax contains no unsaturated alcohols. In 1951 Meier[187a] reported that the acetyl and hydroxyl numbers of carnauba wax alcohols are 105 and 114 respectively, indicating a preponderance of C_{34} alcohols.

Findley and Brown[79] by an improved method of saponification have determined the unsaponifiable of a commercial grade (No. 3 chalky) of carnauba wax to be 51.0 per cent vs. 54.0 per cent as determined by Koonce and Brown on the same wax. They also report the acids (m. 83.5–84.5°C) as 50.0 per cent vs. 43.0 per cent previously reported by Koonce and Brown.

Of the total mols, 2.73 per kg, the hydroxyl group constitutes 2.43 of the composition, leaving 0.30 mols/kilo of hydrocarbons. Since the original wax contained $0.30 \times 0.51 = 0.15$ mols per kilo of hydrocarbons, the percentage weight of hydrocarbons (calc. as $C_{27}H_{56}$) would be 5.7 per cent. The total alcohols in the unsaponifiable by difference would amount to 45.3 per cent,

or lower than the values (48 to 54 per cent) reported by many previous investigators.

Stürcke postulated the presence of an oxy- alcohol derived from the unsaturated alcohol, *carnaubenyl alcohol* (m. 39°C). There are no unsaturated alcohols as such in carnauba wax.

A report of *Revista commerc-italo-brasil*[10] gives the fatty acids as 47.95 per cent for carnauba. They had a melting point of 85°C, a saponification number 79.8–88.3, and iodine number 11.5. Bunger and Kummerow[43] have tried out four different saponification methods, briefly (a) Zweig and Taub, (b) Koonce and Brown, (c) Chibnall *et al.*, (d) solvent modified Koonce and Brown. They obtained 40, 45, 42, and 40 per cent of acids in the hydrolyzate respectively, when analysing the fatty gray carnauba wax. More recently Murray and Schoenfeld[195] determined the fatty acids of Yellow No. 1 wax as 43.4 per cent.

The fatty acids in carnauba wax have a lower number of carbons than do the alcohols, if we except the lactones. The fatty acids combined with higher alcohols as esters were believed to have ranged from C_{24} to C_{32}, but in 1953 Murray and Schoenfeld proved that the normal acids ranged from C_{18} to C_{30}. They fractionated the methyl esters of the normal fatty acids by an amplified distillation method of Weitkamp in a sufficient state of high purity for their sure identification. The relative amounts (per cent) of these normal acids is as follows: C_{18}, 3; C_{20}, 11.5; C_{22}, 9; C_{24}, 30; C_{26}, 12; C_{28}, 16.5; and C_{30}, 7 There is evidence that the normal C_{32} acid does not exist in carnauba. The proportion of normal acids to the total fatty acids of carnauba was found to be 38 per cent. Since the wax contains an optimum of 45 per cent of fatty acids, it would appear that the content of *n*-fatty acids does not exceed 17 per cent, equivalent to 36.5 per cent of *n*-fatty alkyl esters (calculated as myricyl lignocerate).

A large difference between the saponification number of their esters (methylated acids) and the saponification number after acetylation indicated to these investigators the presence of a considerable amount of hydroxylated esters. They were separated from the *n*-esters by adsorption on alumina; they were completely eluted from the column by petrolic ether. The methyl *n*-esters melted at 57–65°C, and had a saponification number of 151. The higher-melting hydroxy acids could be further eluted with benzene-ethanol, toluene-ethanol, and chloroform-acetic acid. It is now doubted that there are any free alcohols in carnauba wax since the high acetyl numbers are accounted for by the hydroxylated esters.

Recently Murray and Schoenfeld [*Australian J. Chem.*, **8**, 437–443 (1955)] isolated seven ω-hydroxy acids from carnauba wax and identified them as *18-hydroxydecanoic*, *20-hydroxyeicosanoic*, *22-hydroxydocosanoic*, *24-hydroxyoctacosanoic*, *26-hydroxyhexacosanoic*, *28-hydroxyoctacosanoic*, and

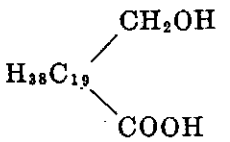
30-hydroxytriacontanoic acids. These hydroxy acids could be reduced to their corresponding diols. 1,30-Tricontanediol (m. 112.8–113.0°C) was new. All of the hydroxy acids are present as ω-hydroxy esters in the wax, inclusive of its estolides of resin acids. These investigators believe the presence of ω-hydroxy esters is responsible for the desirable physical properties of this wax.

A C_{27} acid (m. 82.5°C) was first discovered by Brodie; it was regarded as an isomer of cerotic acid by Stürcke. The normal C_{27} acid, *n*-heptacosanoic, melts at 87°C; hence the acid of Brodie, or Stürcke, was probably an isomer, isoheptacosanoic (m. 82°C) or a eutectic of lower and higher homologs, *hexacosanoic* and *octacosanoic acids.* It is now known that carnauba wax does contain both of these C_{26} and C_{28} acids, as well as some C_{30} acid, and possibly C_{32} acid.

The alcohol-soluble fraction (5.3–6.6 per cent) of carnauba wax apparently consists of a small portion of free waxy acid (3.0–3.5 per cent) and a large proportion of resins. Neutral resins in waxes of this nature generally have a saponification number of not less than 86, and an iodine number of at least 39. Since the alcohol-soluble fraction has an iodine number of 2.27 (on original wax basis), the amount of resins would be $2.27/39 \times 100$, or 5.82 per cent. The saponification number apportioned to resins would be 0.86×5.82, or 5 per cent. Since the saponification number of the wax is about 79, that portion attributable to the normal and hydroxylated alcohol-fat acid esters after deducting resins (6), free acids (3), lactides (6), and combined glycols (1), is 63, indicating an average molecular weight of about 753 for the esters.

The iodine number of the less resinous grades of carnauba wax is relatively low, e.g., North Country No. 3, 7.55 (Hübl). The iodine number of its alcoholic extract is 2.27 (on orig. wax basis). Murray and Schoenfeld recovered 4.6 per cent of a brown resinous material from the acidified aqueous alcoholic liquors, after removal of the acids, by concentrating them to half volume and extracting with ethyl acetate. However the unhydrolyzed resins most likely are somewhat higher.

Stürcke isolated a lactide from carnauba wax, and described it as an anhydride of a polymethylene acid alcohol



from which an acid $(C_{19}H_{38}(COOH)_2$ (m. 90°C) has been prepared. The lactone appears to be a dimeric lactone or double etholide (m. 103.5°C) of *medullic* (heneicosanoic) *acid.* This lactone and long-chain glycols may account for the wide lattice spacing, 83 Å, for carnauba wax, as given by

Kiessig [*Kolloid Z.*, **98**, 213–221 (1943)]. Free cerotic acid in carnauba wax was first identified by Bérard.

Stürcke referred to the presence of a hydrocarbon (m. 59.2°C) in carnauba wax, in the amount of a fraction of 1 per cent. Gottfried and Ulzer[89a] referred to the hydrocarbon as *heptacosane*, $C_{27}H_{56}$ (m. 59.0–59.5°C). Farcy[76] referred to a hydrocarbon content between 1 and 1.62 per cent. Murray and Schoenfeld[195] obtained a hydrocarbon fraction (m. 64.6–65.0°C) which amounted to 0.2 per cent; it had a melting point of 63.0–63.5°C (r.p. 62.6°C) on further purification, although admittedly still impure. They obtained a total hydrocarbons content of 0.7 per cent. The hydrocarbons are probably C_{27}, C_{29}, and C_{31}, with C_{27} predominating.

The presence of an isomer of lignoceric acid, possibly 2-methyltricosanoic acid, was first discovered by Stürcke [*Schaedler Technol. der Fette und Oele*, 2 te Auf., p. 884] who called the acid (m. 72.5°C) *carnaubic acid*. The existence of closely related derivatives, such as *2-methyltricosenoic acid* and its oxidized product *2-hydroxyketotetracosanoic acid* is postulated in accounting for the iodine and acetyl numbers of the wax.

A C_{27} acid (m. 82.5°C) was first discovered by Brodie; it was regarded as an isomer of cerotic acid by Stürcke. The normal C_{27} acid, *n*-heptacosanoic, melts at 87°C; hence the acid of Brodie, or Stürcke, was probably the isomer, isoheptacosanoic (m. 82°C), or a eutectic of lower and higher homologs, *n*-hexacosanoic and *n*-octacosanoic acids.

The alcohol-soluble fraction of carnauba wax apparently consists of a small amount of free waxy acid (3.0–3.5 per cent) and some resin. Murray and Schoenfeld[195] recovered 4.6 per cent of a brown resinous material, possibly resin acids, from the acidified aqueous alcohol liquors, after removal of acids, by concentrating them to half volume and extracting with ethyl acetate.

The hydroxy acids in carnauba wax are both saturated and unsaturated. It is postulated that the saturated hydroxy acids are ω-hydroxy acids and capable of forming etholides (acid-alcohols), and that the unsaturated hydroxy acids are capable of forming resinous constituents, and are responsible for the fairly high iodine number of the wax.

Carnauba as "Melting Point Booster." Carnauba wax is used extensively to elevate the melting point of other waxes, and so is known as "melting point booster." Lewkowitsch has recorded the melting points of mixtures of stearic acid, ceresin, and paraffin wax, each with carnauba wax, on the basis of values obtained by Valenta[297]. As Valenta's values on paraffin-carnauba melts were determined with a high-melting paraffin [60.5°C (140°F)], new values were obtained by Bulatkin[310] on paraffin of 54.4°C (130°F) melting point, since this is the kind commonly used in America.

Measurements were made in a manner that would accurately deter-

TABLE 38. ELEVATION OF MELTING POINT OF PARAFFIN BY CARNAUBA WAX

Carnauba Wax (%)	Paraffin (%)	Melting Point (°C)	Melting Point (°F)
—	100.0	54.4	130.0
1.25	98.75	62.2	144.0
2.5	97.5	76.6–75.8	170.0–168.5
5.0	95.0	79.3	174.7
7.5	92.5	78.5	177.0
10.0	90.0	81.1–78.5	178.0–177.0
20.0	80.0	81.4	178.5
30.0	70.0	81.4	178.5
40.0	60.0	81.7–81.1	179.0–178.0
50.0	50.0	81.4	178.5
60.0	40.0	81.7	179.0
70.0	30.0	81.9	179.5
80.0	20.0	82.2	180.0
90.0	10.0	83.3	182.0
100.0	—	85.5	186.0

mine the shoulder of the curve which lies between the values of 1.25 and 10.0 per cent of carnauba, in the carnauba-paraffin wax melts.

The table shows that the main boost in melting point of paraffin may be made with as low as 2.5 per cent of carnauba wax, namely from 130 to 170°F. There is not much occasion to increase the carnauba beyond 3 per cent, which will give a wax blend having a melting point as high as 172.5°F.

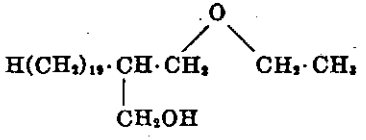
In these mixtures the waxes with a high percentage of carnauba wax have a high shrinkage value. Casts made with a high carnauba wax content, that is, over 50 per cent, are quite strong. Those ranging from 40 to 20 per cent of carnauba are weak; the crystallizing forces counteract one another, and this peculiarity is noticed in the melts. There appears to be one mixture of the two waxes, i.e., paraffin and carnauba, in which these forces balance, and that is with about a 15 per cent of carnauba. Below 10 per cent of carnauba the wax compositions are strong.

Under water the softening points of carnauba-paraffin blends are considerably below their respective dry melting points, and this factor proves highly disadvantageous when the blended wax is to be used to coat paper containers that come into contact with hot liquids. Carnauba and paraffin form a mixture which is not a true solution, and it is generally believed that the resinous constituent of the carnauba more or less covers the particles of the lower-melting paraffin, thus boosting the dry melting point. Separation of carnauba constituents from the paraffin mixture is frequently noted in handling the blended wax.

White Carnauba Wax. It is practically impossible to bleach carnauba wax white without altering its composition. There is a demand for white carnauba wax for use in cosmetics, or other purposes where whiteness is a

TABLE 39. APPROXIMATE COMPOSITION OF CARNAUBA WAX

Alkyl Esters of Wax Acids: 84–85%
Simple esters of normal acids, 5–6%
Ceryl arachidate, and behenate, 1%
Montanyl, myricyl, and lacceryl lignocerate, 2.5%
Lacceryl cerotate, 0.5%
Geddyl lignocerate, montanate, and melissate, 1%
Acid esters, C_{18}–C_{30} 5–6%
Diesters, 19–21%
Esters of hydroxylated acids, 53–55%
Saturated, 38–40%
Ceryl-ω-hydroxycerotate, and -ω-hydroxymelissate
Myricyl-ω-hydroxymelissate
Esters of C_{18}, C_{20}, C_{22}, and C_{28}-ω-hydroxy acids
Unsaturated, 14–16% (Iodine no. 5.3–5.5)
Free Wax Acids: 3–3.5%
Carnaubic acid
Cerotic acid
Lactides: 2–3%
(Dimeric) ω-1-lactone (m. 103.5°C) of hydroxymedullic acid
Free and Combined Polyhydric and Oxy-Alcohols: 2–3%
Dihydric pentacosanol, $C_{23}H_{46}(CH_2OH)_2$ (m. 103.6°C) (Now considered to be a mixture of $< C_{22}$, C_{22}, C_{24}, C_{26}, C_{28}, and $> C_{28}$ diols)
Oxy-alcohol derived from carnaubenol, $H(CH_2)_{19}\cdot CH(CH_2OH)\cdot CH{:}CHCH_2$ (m. 39°C)



Resins (alcohol soluble): 4–6%
Hydrocarbons: 1.5–3%
Heptacosane (m. 59.2°C), nonacosane, and hentriacontane
Moisture and Mineral Matter: 0.5–1%

prime need. White carnauba wax may be prepared by several methods. (a) The carnauba is mixed with paraffin, the temperature raised to about 220°C, and activated carbon, or "Tonsil" clay, is added. The whole is then filtered. (b) Carnauba is fractionally crystallized from its benzin solution at 16°C, when crystals (m. 80.8°C) of pure white color are collected, together with a by-product wax (m. 60°C). (c) Crude carnauba wax is dissolved in boiling butanol and treated with metallic sodium, the effect of which is to bleach the wax. The solution is then filtered and the solvent recovered. (d) The carnauba wax is mixed with paraffin, then saponified with alkali. The saponified mixture is then boiled with water, and the white wax separated as a layer from the aqueous soapy solution. The last described method, which is of German and Austrian origin, permits the

utilization of the cheap lower grades of natural wax. The white wax is nonsaponifiable, or nearly so, and has a very low viscosity when melted.

What is known as "carnauba residues" is obtained by acidifying the soap solution of method (d). The residues have a melting point which ranges between 67 and 72.5°C; and acid value of 21.5–22.2; an ester number of 7.3–12.2; and a saponification number 32.2–38. The bleached wax has an acid value of 0.6–0.4; an ester number of 7.4–9.2, and a saponification number of 7.8–9.8.

Uses of Carnauba Wax. Carnauba wax has been called the main-spring of the floor-polish industry, and no entirely satisfactory substitute has been found for this wax. The value of the carnauba constituent in polishes lies in the fact that it produces the most durable luster and hardness. *Candelilla*, *ouricury*, and *sugarcane wax* have been used to some extent as substitutes, but are inferior. *"Gersthofen Wax OP"*, a synthetic ester wax of very high melting point, has been used in floor polishes, but must be used in conjunction with carnauba. The OP wax has very great oil-absorption power which is an important requirement in the paste polishes. "A-C Polyethylene" and other synthetic waxes find uses as partial replacements for carnauba wax in furniture and other polishes

Carnauba with montan wax is used for the recording records on phonographs, as the mixture will take a very fine tonal impression, which can then be transferred to copper by plating to produce the master record. Carnauba wax is used in the formulations of the wax foundation of carbon papers. Shoe creams with a characteristic "ring formation" on the surface due to the *myricyl alcohol* of the carnauba wax are much sought after in the trade.

Carnauba wax is used in leather dressings. It is used as a hardening agent in candle compositions. A considerable amount of carnauba is used for the manufacture of cheap artificial *ceresins*, which usually employ 5 per cent or less. Carnauba has certain advantages for electrical use because of the great shrinkage that it undergoes in passing from the liquid to the solid state.

Carnauba wax enters into the manufacture of photographic films, chalk, matches, soap, unguents, dry batteries, citrus fruit wax dips, etc., the carnauba being generally used in conjunction with other waxes. Carnauba is used for staining interior woodwork. One pound of carnauba wax is dissolved in a gallon of toluene and a colored dye is added in an amount sufficient to give the desired staining effect.

Grades of Carnauba Wax Commercially Available. The principal grades of carnauba wax offered in the New York market and their prices for December, 1941 and 1949 were as follows:

Grade	Price in Bag Lots 1941	1949
#1 Yellow	$0.82	$1.12
#2 Yellow	.80	1.10
North Country #3 (crude)	.74	.83½
Chalky	.70	—
Refined NC #3	.81½	.87½

The greater demand on the Brazilian shippers was for the North Country #3, and the Refined #3. The latter is offered in flakes as well as in chunks.

Consumption of Carnauba Wax. Sweet[267] lists the consumption of carnauba wax in the various industires as follows:

	Consumption (pounds)	Amount (pounds)	Grade Used
"No-Rub" wax emulsion—floor polish	5,760,000	2,680,000	No. 3
		1,580,000	No. 2
		1,500,000	No. 1
Leather dressing and shoe polish	4,480,000	3,000,000	No. 3
		480,000	No. 2
		1,000,000	No. 1
Paste and liquid polish for floor and auto	2,240,000	1,680,000	No. 3
		560,000	No. 2
		1,000,000	No. 1
Carbon paper coating	1,920,000	1,000,000	No. 3
		920,000	No. 2
Paper sizing and polish	480,000	480,000	No. 1
Paper impregnating, bottle caps, etc.	320,000	320,000	No. 3
Miscellaneous	800,000	500,000	No. 1
		300,000	No. 2

The total exports of carnauba wax in 1939 were approximately 11,000 short tons, of which the United States took about 55 per cent. The imports into the United States in 1941 were about 11,000 short tons, but fell off somewhat in the years 1942 to 1945. In 1945 the importations were 14,773,000 pounds valued at $9,854,000, and in 1950 importations increased to 18,000,000 pounds valued at $15,120,000. Parnahyba is the chief port of shipment for carnauba wax. Prices of importations have fluctuated from a low of 65 cents to a high of $1.60 per pound during the last decade of years.

Caranday Wax

The carandá palm, *Copernicia australis* Beccari (*Corypha cerifera* Mart.), of the family Palmae, has large fronds, which are thinly coated with wax. The carandá palm grows profusely on the river banks and in swamps of Mato Grosso, Brazil. It also grows in the northern part of Paraguay in the vast plain which extends from the west bank of the Río Paraguay to the

eastern foothills of the Andes. Markley[175a] refers to the palm as the *caranday* palm, and points out that the prime difference between the Gran Chaco and the sertão plains of northeastern Brazil is that normally the periods of draught are shorter in the Chaco, which is essentially a low-lying country of little elevation and less relief, and large regions are inundated during the rainy season.

The caranday palm averages about 30 feet in height, and has a trunk 7 to 10 inches in diameter; it resembles the carnauba (*C. cerifera*) of northeastern Brazil, but the mature caranday leaf is composed of 48 leaflets with numerous red dots, whereas the carnauba leaf is composed on the average of 60 leaflets with dots almost absent. Selected leaves give 3.5 to 4.4 g of clean wax; unselected leaves average less than 3.0 g of wax per leaf.

According to Markley[175a] the firm of Carlos Casada Ltda. (quebracho processors in the Chaco) became interested in the commercial exploitation of the carandá palm as a source of wax, and in 1949 erected a pilot plant for recovery of the wax. Another firm 70 miles further north also erected a pilot plant. As a result, in 1950, 1297 kilos of caranday wax were imported into the United States, but the price of 75 cents per kilo, f.o.b. New York, received was too low to make its economic recovery satisfactory, and the pilot plants closed down.

In these pilot plants, the leaves were first dried, either in a special drying house or outdoors. Various types of machines were used for recovering the wax. The light gray, fluffy powder was removed from the leaves by aspiration with air while the latter were being beaten or cut in the machines. The aspirated wax powder accumulated in a closed room or bin, into which the aspirator duct led. The crude wax powder was melted with direct steam and hot water and the extraneous dirt and leaf trash separated by centrifuging. The separated liquid was run into large shallow pans where the water and wax separated into two layers as the wax slowly solidified. After cooling, the cakes of hard wax, 0.75–1.5 inches thick, were broken into irregular pieces and bagged prior to shipment. In another process the powder was first purified by bolting through fine cloth or woven wire screen before it was melted by indirect steam; it was also filtered prior to running into the solidifying pans.

When fractured, the hard dense wax exhibits a yellowish-green to light-brownish-green color. It is readily bleached to a pale tan color by a little benzoyl peroxide, and to a pale cream color by hydrogen peroxide-chromic-sulfuric acid. The wax is superior to ouricury and comparable to the higher grades of carnauba wax. The Mato Grosso wax, according to Madeiros Transcoso[278], has a specific gravity (d^{25}) of 0.990, acid value 9.5, acetyl value 40, iodine number 8.0, saponification number 64.5, melting point (drop) 84.5°C, melting point (cryoscopic) 79.7°C; its moisture content is

0.9 per cent, its ash content is 0.18 per cent, and its acetone-solubility (at 25°C) is 2.7 per cent. The Paraguayan wax, according to Findley and Brown[79], has a melting point of 74–81°C, acid value 5.0, ester value 73.5, and iodine number 8.9. The hydroxyl number is 36.5. The mean molecular weight of the wax is 671.

By the use of functional group analysis and fractionation by molecular distillation, Findley and Brown[79] have calculated the unhydrolyzed caranda wax to contain the following mols per cent of constituents: esters 44, hydroxy esters 9, acid esters 1, diesters 16, free alcohols 26, free acids 4, and hydrocarbons 1. About 14 per cent of the esters distil at 150°C, and the remaining 86 per cent at 250°C under 0.2–2.0 microns (Hg) pressure. About 46 per cent of the hydroxy acids distil at 250°C; the remaining 54 per cent are found in the residue, together with acid esters and diesters. They estimated that 41 per cent of the total fatty acids in caranda wax are hydroxy acids. Caranda wax contains about 43 per cent of total fatty acids, and 14–15 per cent of free alcohols, probably resinols.

Knaggs[123] who visited the Mato Grosso area stated that because of transportation difficulties and scarcity of labor in the areas where the carandá grows, it does not appear that the Brazilian wax will be available commercially for some time to come. Many of the largest stands of this palm are adjacent to the Río Paraguay, on which regular boat service is maintained. Roads, trails, and narrow-gauge railroads extend from the river into the Chaco at various points, making it possible to cut and process caranday leaves if labor supply were only available[175a]. It has been said that the carandá palm can be grown in southern California and in southern Florida.

Wax of Saw Palmetto

A wax is obtainable from the leaves of the saw palmetto, *Serenoa repens* Bartram, a small palm which is widely distributed in the southeastern and southern states, ranging from South Carolina to the Florida Keys and along the Gulf Coast to Louisiana. Wax was obtained by Wilder and Kitzke by brushing the sun-dried leaves and also extracting them with heptane. The wax is hard, brown in color, and somewhat resinous in appearance. It has a melting point of 81.2°C, acid value 16.3, saponification number 101.5, iodine number 9.8, and needle penetration (100 g/5 sec) < 1. The wax contained about 13 per cent of resinous material, half of which was soft and tacky and could be leached out by acetone, and the other half hard and insoluble in boiling isopropyl alcohol. The yield of wax was 4.9 per cent on the dried leaf basis.

Wilder and Kitze state that the gel formation that occurs with a precipitation temperature of 98°C in naphtha is firm, although it is grainy and has poor solvent retention, which makes saw palmetto wax deficient

for use in naphtha-type polish products. [Wilder, E. A., and Kitzke, E. D., *Science*, **120**, 108–109 (1954).]

Colombian Palm Wax

Colombian palm wax is a resinous type of wax obtained from the leaf stems of the wax palm, *Ceroxylon andicola* Humboldt, or allied species of Ceroxylon, belonging to the Arecinea tribe of palms, family Palmae. *C. andicola* grows extensively in New Grenada. A naturalist states "Try to imagine a palm having a cylindrical, smooth, shining, alabaster-like trunk which rises, shaft-like, 200 feet or more straight into the air and bears at its summit a crown of feathery, silvery-green leaves, nearly 20 feet in length. Then visualize it standing either solitary or in company with others of its kind at nearly 10,000 feet above sea level, within sight of perpetual snow." The tallest of all palms is the Quindio wax palm of the Quindio Pass of the Andes mountain range in Colombia. Wendland, the botanist, named this species *Ceroxylon quindiuense*.

Another species of wax palm growing at the boundary line between Colombia and Ecuador has furnished some commercial palm wax. This species averages 40 to 50 feet in height, and grows at an altitude of 13,450 feet above sea level; it is known as the Salento wax palm, *C. ferrugineum* Andrews. Still another species is the Santamarta wax palm, *C. ceriferum*. The natives call these palms *palma de cera* (wax palm). The genus name, *Ceroxylon*, comes from the two Greek words, *keros* (beeswax) and *xylon* (wood); the specific term, *andicola*, means "of or belonging to the woods." It was in 1801 that Alexander von Humboldt, the renowned naturalist, discovered the first species of wax palm.

To recover the wax it is scraped from the trees, but sometimes the palms are felled first. Upon the trunk of the tree, in the rings left by the fall of the leaf stems, the wax is about one-sixth of an inch thick. It is in the form of a greenish-white powder, and is gathered and melted down over a fire. Thorpe[274] states that the wax is obtained by felling the tree and scraping off the coating, which is then boiled with water; thus softened, the wax floats to the surface and impurities are removed. It is made into little balls and dried as well as bleached in the sun. One tree is said to yield 25 pounds of wax.

The palm wax obtained from the Indians is yellowish-white, porous, and friable. When melted it is a dark yellow, slightly translucent, and fragile like resin. It is partly wax and partly resin, and is said to become highly electrostatic by friction. If the mixture is dissolved in hot alcohol and the wax fractionally separated or freed from resin, the purified wax has a much lower melting point. Palm wax according to Vauquelon, contains two-thirds of a resinous substance and one-third of pure wax constituents. The article of commerce, known as "palm wax," is refined from the crude wax after the

latter has been exported; refining is conducted by means of solvent extraction. The wax then contains about 37 per cent of resinous substance (resinols).

The crude wax contains moisture 1.5 per cent, ash 0.6 per cent, non-wax solids (insol. in $CHCl_3$) 6.5 per cent[11]. When refined it has a specific gravity (d^{15}) of 1.018, acid value 19.8, saponification number 73.7–104.4, and iodine number 32.8. It melts at 93°C. The wax is soluble in cold chloroform, carbon tetrachloride, and benzene; it is not soluble in cold alcohol, ether, or petrolic spirit; it is soluble in hot oil of turpentine. The refined wax is brown in color. The constituents of palm wax consist of wax acids combined with alcohols to form esters, free wax acids, hydrocarbons, and resin. The high melting point and specific gravity indicate that the wax contains a considerable proportion of hydroxy acids and/or etholides. The resin may be separated from the wax by solution in alcohol; it melts above 100°C, and is said to have the composition $C_{20}H_{32}O$[274].

The natives use the crude wax to make tapers, since it burns with a clear, bright flame. It has been said that the wax cannot be fully refined by chemical bleaching, or otherwise without the addition of paraffine. The melting point is nearly in direct proportion to the amount of paraffine added, particularly after a few per cent has been used. The refined wax has been used in America mostly as a "replacement" wax for carnauba (see also Commercial Palm Waxes).

Commercial Palm Waxes

The palm waxes of commerce are so-called "replacement waxes" for carnauba wax. The commercial palm wax, when free from paraffin, is, generally speaking, a resinous wax of olive-brown color, and not unlike licuri wax (*Cocos coronata*). It has a durometer hardness of 100 at 15°C, and 97 at 25°C. It begins to sinter and soften at 74–75°C in a capillary tube, and melts at about 85–86°C to a viscous liquid. It has a density of 1.0464 at 9°C, and 1.0447 at 16°C. Its coefficient of cubical expansion is 0.00023. The wax has an acid number of 10.6, and iodine number of 16.9 (Hanus), and a saponification number of 103.9. It is said that the wax cannot be refined by chemical bleaching or otherwise without the addition of paraffine.

Palm waxes in the New York market are not in any sense genuinely derived from the sources described. They are generally considered as "replacement" waxes to be used in the arts in place of the more expensive carnauba wax. They are prepared by blending some of the harder and more resinous vegetable waxes with paraffin; for example, paraffin is blended with "refined palm powder," which latter has a melting point of 112°C. With 75 per cent of paraffin added, the wax is of yellow color and melts at 80°C (176°F). White palm wax consists mostly of paraffine.

The following table shows the changing properties of a palm wax prepared

from a paraffin-free palm wax (m. 86°C) and added paraffin wax (130/132°F—AMP)

Per Cent Paraffin	M.P. (°C)	Density (d^{15})	Hardnes (Durometer)	Acid Value	Sapn. Number	Iodine Number
10	85	0.9950	96	14.8	94	13.0
30	83	0.9760	88	11.2	70	8.4
65	77	0.9430	74	5.6	28	3.8
90	69	0.9190	64	1.0	10	1.2

The following analyses were made of commercial specimens.

Color	M.P. (°C)	Density (d^{15})	Hardness (Durometer)	Acid Value	Sapn. Number	Iodine Number	% Paraffin Indicated
Pale brown	82.2	0.9950	92	3.84	29.0	2.54	24–30
Yellow	80.0	0.9510	77	4.42	31.0	2.76	57–65
White	71.1	0.9050	60	—	—	—	87–89

The specimen of yellow wax was ostensibly a blend of semirefined palm wax (m. ca. 86°C) and paraffin. The low iodine number of the pale brown wax indicates that it may have been a blend of candelilla and paraffin waxes.

Since the melting point of the darker grade of commercial palm wax is high, because of the high hydroxy acid and resinol contents, it will greatly elevate the melting point of ordinary paraffin. For example, when 2 per cent of palm wax is added to paraffin (130/132°F—AMP), the blend will have a melting point of 138°F (58.9°C). When 5 per cent is added, the melting point is elevated to 147°F (64+°C). Palm waxes have a pleasing odor, somewhat different from carnauba, and are of sweetish taste. Added to ceresin, commercial palm wax will prevent oxidation of the hydrocarbons when the ceresin is subjected to continuous heating. White commercial palm wax is the equivalent of a cheap artificial ceresin.

Ouricury Wax

Ouricury wax, also known as *ouricuri*, uricury, and uricuri, is a wax derived, according to Ivanovsky[117], from the undersurface of the leaves of a tall palm, *Attalea excelsa* Martius. *Attalea* species of the Cocoineae tribe of palms are tall trees, growing from the mouth of the Rio de la Plata to Honduras, especially along the Amazon River. The heavy fruit of *A. excelsa* (also reclassified as *Scheelea martiana* K. & D.) is egg-shaped, and brown or greenish-brown in color. The natives call it "dupras"; it contains several edible seeds, 2–5 cm long and 1 cm thick, chocolate-brown outside, white inside. These contain a vegetable tallow. A related species, *A. funifera* Mart., the Bahia bast palm, furnishes fiber known as piassava for cordage.

The identity of the one or more species of palm furnishing ouricury wax has not been fully established, since *Syagrus coronata* Becc. of Kew Botanical Gardens has been referred to as the uricury wax palm and Rowan refers to *Cocos coronata* Mart., a species of syagrus coconut, as the botanical source of ouricury wax, a view which is shared by Knaggs[128]. The syagrus coconut grows in north and east Brazil. This species (according to Silva,

Rio de Janeiro), produces "Ouropaido wax" (licuri wax) which is not the same but appears to be closely related to ouricury. According to Knaggs, the native of the southeastern section of the State of Bahia had freely used burning licuri leaves to exterminate ants, without realizing a potential market outlet for the wax which could be scraped from the leaves.

The ouricury wax palm grows to a height of 18 to 30 feet, and the fronds arch out from the thick crown; the leaves grow to 10 feet in length. Each palm yields an average of ten wax-producing leaves a year. The fruit hangs in clusters, and the fibrous central portion investing the hard shell corresponds to the fleshy portion of a plum, while the shell or nut corresponds to the stone of stone fruits, the seed being the kernel. The pulp of the ripe fruit serves as an excellent food, and the green fruit when cooked is edible. The seed can be expressed for oil or vegetable tallow which it contains.

Since the wax clings tenaciously to the leaf it is customarily scraped off with a knife or with bits of broken glass, and is collected in the form of a powder. This powder, representing 0.48 per cent of the dry leaves, contains a great deal of fiber from the leaves, as well as dirt; this inert material is then removed by mechanically moved sieves. After being melted in a rotating melting pot heated by circulating hot water, the wax is run into forms, cooled, and solidified in small blocks. These blocks are then sacked for export. This grade which since 1938 has been known as "machine-processed" ouricury wax is very hard and in color is not unlike the darker grades of carnauba wax. In general, ouricury is a dense, hard, brittle, yellow wax.

It has been reported that a refined quality of ouricury, known as "Brazilian double-refined" wax, is prepared by digesting the scrapings of the palm in a caustic soda solution with the aid of steam; the vegetable matter sinks to the bottom of the tank and the wax, freed from an appreciable amount of plant resinous material, rises to the top in the operation as the water is boiled off. The high specific gravity of the wax does not permit its separation from the plant material in the usual way in which waxes are separated. The refined wax as above prepared comes into the market in the shape of blocks, and is characterized by its low saponification number.

Properties of Ouricury Waxes. The physical and chemical constants of the ouricury waxes are as follows:

	Ouricury Natural (*A. excelsa*)	Double Refined (Brazilian)	Licuri Natural[171] (*C. coronata*)	Licuri Refined (Brazilian)
Density (d^{15})	1.0685	1.0561	1.0100	0.9980
Density (d^{25})	1.0661	1.0535	—	—
Melting point (°C)	84.3	79.0	84.5	83.8
Solidifying point (°C)	72.2	68.9	—	—
Acid value	23.8	21.1	12.0	3.4
Saponification number	85.3	61.8	109.2	85.8
Ester value	61.5	40.7	97.2	82.4
Iodine number (Hanus)	7.1	6.9	15.2	7.8
Ash (%)	1.91	0.55	—	—

Lüdecke[168] gives the following properties of crude and purified ouricury wax:

	Crude Wax	Purified Wax
Density (d^{15})	1.068	1.056
Melting point (°C)	82–83	79–80
Solidifying point (°C)	73	71
Acid value	16–22	12–20
Saponification number	78–92	66–77
Ester value	62–70	54–57
Hübl ratio (ester val. acid val.)	3.5	3.5
Iodine number (Hanus)	6.3–8.0	6.2–7.5
Hydroxyl number	130.0	131.2
Buchner number	0.99	1.04
Ash (%)	2.1–3.2	0.6–0.8
Free resin content (%)	5.8–6.2	4.7–5.5
Unsaponifiable (%)	26.0–31.0	28.0–34.5
Moisture (%)	1.2	0.3

Findley and Brown[79] report the following constants for the acid, ester, hydroxyl, and unsaturated groups of the unhydrolysed ouricury wax: acid number 28.6, ester number 84.1, hydroxyl number 62.3, and iodine number 16.0. They also give the wax constituents of the unhydrolysed wax as hydrocarbons, free alcohols, free acids, esters, hydroxy esters, and acid esters. Because of the change in composition during the distillation, the compositions of these fractions could not be combined to give the true composition of the original wax, except for the hydrocarbon content which was found to be 7 mols per cent.

A "fatty" grade of machine-processed ouricury wax had a melting point of 87°C, acid value 71, saponification number 110, iodine number 17.2, and durometer hardness 100. The very high acid value and iodine number indicate that the specimen examined had a high resin content, possibly as high as 15–19 per cent. American refined ouricury is the designation given to the crude wax which has been remelted and filtered to remove mineral and foreign matter. It is produced and marketed in both lumps and flakes. If ground to powdered form the wax may be levigated with water and the mineral and fiber impurities separated. The flakes have a melting point of 83.3°C, the melt solidifying at 72.9°C. The great spread between the melting and solidifying points is characteristic of the ouricury waxes, a property which is not found in carnauba wax. Lüdecke has given the melting point of refined ouricury wax as 80–82°C, and the solidifying point as 71°C. The saponification number of a specimen of flakes was 108.

Ouricury wax, crude, has a cubical expansion coefficient of 0.000244 at 25°C, and 0.000604 for the melt[311a]. The refined wax has a cubical expansion coefficient of 0.000361 at 25°C and 0.000668 for the melt. The shrinkage of

ouricury wax in its transition from the molten to the solid state (25°C) appears to be greater than that of other known waxes. The cubical expansion coefficient of the solid crude wax, namely 0.000244, is also lower than that of any other.

Ouricury wax is sparingly soluble in the polar solvents, such as alcohol and acetone, and only partly soluble in the nonpolar solvents, such as benzene, carbon tetrachloride and chloroform in the cold. The wax is soluble to the extent of 0.350 gram in 100 ml of ethylene chloride at 37°C. The raw wax when dissolved in benzene leaves a residue of 8.5 to 11 per cent, and the purified wax 3.8 to 5 per cent, at 25°C[168]. In acetone the unextractable residue amounts to 58 per cent. In its solubility in solvents it differs little from carnauba wax.

Ouricury and licuri waxes have a fragrant odor, resembling that of carnauba, but not as fragrant or agreeable. The wax, when powdered, produces a yellow-orange color with a 10 to 20 per cent solution of NaOH, or red coloration with a 25 per cent solution of KOH; carnauba, on the other hand, produces a colorless solution (motta test).

All of the waxes from the Cocoineæ tribe of palms are believed to contain substantially the same constituents, in proportions but slightly modified. They contain *myricyl cerotate*, free *cerotic acid* and its higher homologs, acid resins, resinols, hydrocarbons, and a very small amount of mineral matter. De Souza Machado[171] reported *cerotic acid* and *melissyl alcohol* as components of licuri wax (*Cocos coronata*). He has given the total wax acids content as 47.34 per cent, higher alcohols as 51.4 per cent, and undetermined as 1.26 per cent.

Schuette and Khan[246] have isolated a wax alcohol (m. 86–87°C) which they believed to be *melissyl alcohol* (m. 85.8–87°C). They also reported having isolated a crystalline acid (m. 79–80°C, neutr. equiv. 140) (corresponding to *hexacosanoic acid*, neutr. equiv. 141). Their findings indicated that the wax ester, *melissyl cerotate* (myricyl cerotate), is the chief component of ouricury wax [*J. Am. Oil Chemists' Soc.*, **30**, 126–128 (1953)].

Although *hentriacontane* has been reported as the chief hydrocarbon of ouricury wax, these investigators report the presence in the commercial ouricury wax of hydrocarbons within the range of C_{24} to C_{36}. They claim that the physical constants of two of the molecular distillates of hydrocarbons separated with the aid of column chromatography identify them as *n*-paraffins C_{24} and C_{30}. A third distillate they presumed to be a mixture of C_{26} and C_{28} *n*-paraffins, and a fourth to be a mixture of C_{32}, C_{34}, and C_{36} *n*-paraffins. The hydrocarbon obtained from a molecular distillate No. 1 gave a melting point of 51.1–51.3°C and a long spacing of 32.6 Å, and that from a molecular distillate No.2 a melting point of 65.6–65.8°C and a long crystal spacing of 40.0 Å.

The approximate composition of a double refined ouricury wax appears to be about as follows: simple esters (e.g., *myricyl cerotate*) and hydroxy esters (e.g., *myricyl hydroxycerotate?*) total 61 per cent, free wax acids (C_{25}, C_{28}, C_{30}, C_{32}) 11 per cent, resin acids 4.1 per cent, resinols 14–16 per cent, hydrocarbons 7 per cent, mineral matter 0.5 per cent, volatile matter 1 per cent. The hydrocarbons are within the range of C_{24} to C_{36} *n*-paraffins. The hydroxyl value for the wax is so high that it indicates that the wax acids include hydroxy acids such as *hydroxycerotic acid*, aside from the resinol components. Findley and Brown[79] stated that they believed that ouricury wax contains appreciable amounts of hydroxy acids, free and combined as *estolides*, resulting in decomposition when an attempt is made to fractionate the wax by molecular distillation.

Uses of Ouricury Wax. Ouricury wax is used as a substitute for carnauba wax in the preparation of floor waxes, shoe creams, and other polishes, although it is inferior to carnauba in producing luster. According to Wilder[322a] (S. C. Johnson & Son, Inc.) crude ouricury wax may be refined for polish use by blending 25 per cent by weight or more in a light petroleum naphtha solvent, filtering it to separate dirt, leafy matter, and resinous material. The refined wax can then be blended up to 16 per cent of the total without affecting the gel strength. Wax mixtures may be made of the refined ouricury, carnauba wax, paraffin, beeswax, and naphtha in suitable proportions.

Ouricury is of value in the inks used in producing typewriter carbon papers, as it provides a means of securing sharp definition of type in copy. In paste-polishes the use of ouricury wax as luster-producing hard wax generally requires revision of the basic formula, other than directly substituting it for carnauba. Ouricury, like carnauba, can be used as a "melting point booster" for paraffin waxes. When 2 per cent of this wax is added to paraffin, the melting point is elevated from 54.4 to 71°C (130–160°F), and 5 per cent raises the melting point to 79°C (174°F). In this respect, ouricury wax behaves similarly to carnauba.

It has been reported that ouricury wax is of value in the finishing of bombing and fighting planes, on account of the high polished durable surface that can be produced with it. This treatment renders the plane surfaces resistant to air friction, and to wetting and condensation.

Economic Value of Ouricury Wax. Initially appearing in export statistics with only 3,075 kg in 1937, ouricury wax contributed 1,341 metric tons to wax exports during the first nine months of 1941. In 1942 machine-processed ouricury wax was offered at 32 cents per pound, f.o.b. Bahia, Brazil, and considerable tonnages have been shipped from Brazil to the United States.

According to the U. S. Department of Commerce, it is estimated that

44 per cent goes into carbon paper; 35 per cent into floor, furniture, and auto polishes; 12 per cent into packaged shoe polishes; and 9 per cent into miscellaneous uses. For the period of 1943 to 1953 the average imports of ouricury into the United States have been 2,586,000 pounds, with an average cost of 57 cents per pound. The refined wax in bags averaged 75 cents per pound in price. Present production and prices are slightly above the ten year averages.

Raffia Wax

Raphia is a small genus of pinnate-leaved palms of the tribe Lepidocaryeæ, family Palmae. The raffia palms are trees with stout trunks, very large spiny leaves, and spicate infloresences, often six feet in length; they bear a spring fruit which contains a single hard seed. They are natives of tropical Africa and South America.

The Madagascar raffia palm, *Raphia pedunculata* Beauvois (*Raphia ruffia* Martius), and the African bamboo palm, *R. vinifera taedigera* K. & D., furnish the fibrous material known as "bass" which is used by florists and gardeners, and which also is of economic value in basketry. The products of the *Raphia* are customarily spelled "raffia." The raffia fiber is obtained from the leaf stalks of the fronds; it is the epidermis of the upper side of the palm leaf. The dull undersurface of the leaf is glaucus, covered with a whitish layer of wax, which can easily be rubbed off.

Thorpe[274] has described the method economically employed in obtaining the wax of the raffia palm. After the bass is removed, large quantities of leaf residues are available as a source of wax. The residues are spread out to dry in cloths in the open air, but adequately sheltered to prevent the wax from blowing away. After drying two to four days the wax coating becomes opaque white, and is detached as a powder by shaking and rubbing the leaves manually. Thorpe relates that ten leaves of medium size, namely 3½ to 4½ meters in length, weighed 104.5 kilograms. From these leaves could be obtained 9.2 kg of bass, which yielded 4.6 kg of clean fiber. The refuse in the green state amounted to 32.5 kg, which when dried left 11.0 kg of leaf residues for wax recovery.

The wax powder removed from the leaf residues is collected, freed from foreign matter by sifting, and then put into boiling water; the wax melts and floats on the surface; earthy impurities settle to the bottom. The melted wax is separated and allowed to solidify. From 11.0 kg of dried residues may be obtained 0.81 kg of crude wax, or 0.78 kg of refined wax. Hence a yield of a trifle less than three-fourths of one per cent based upon the original weight of leaves taken from the palm is obtained.

Raffia wax is a hard light-brown wax which can be easily pulverized. It is possible to bleach it by levigating the powdered wax with water con-

taining a little chromic acid. Excessive amounts of chromic acid tend to impair the hardness of the wax. The natural wax melts at 82.5°C, and has a density (d^{15}) of 0.950. It has a specific gravity ($d^{99}_{15.5}$) of 0.832 to 0.836 when melted. Haller found that the wax could be distilled at 280–300°C under 100 mm pressure, with some decomposition.

Thorpe[274] gives the acid value of raffia wax as 4.9–6.5, saponification number 51.3–50.3, and iodine number 7.7–10.7. The wax is slightly soluble in alcohol, ether, acetone, chloroform, and petrolic ether. It dissolves well in boiling benzene, and in boiling ethanol although about 10 per cent separates out on cooling. The chemical composition of raffia wax is not fully known. Its chief constituent is *raphia alcohol*, $C_{20}H_{41}OH$, which appears to be an isomer of *n*-arachidyl alcohol. It is probable that raffia wax has both hydrocarbons and alcohols of appreciably higher than C_{20} as components.

Wax of North Madagascar Doumpalm

Madagascar palms of the branching fan-type, Borasseæ tribe, locally known as "satrabe" (*Medemia nobilis* Hild. et Drude), and "satramira" (*Hyphaene schatan* Boj.), contain a little less than 1 per cent of wax in the stem, petiole, and lamina. The waxes however have not been recovered from these palms on an economic basis.

(2) Waxes of Shrubs and Herbs

A few shrubs and herbs are one of the important economic sources for the natural vegetable waxes of commerce, such as *Euphorbia antisyphilitica*, and *Pedilanthus pavonis* which yield candelilla wax. Many species of the genus *Euphorbia* contain both resin and wax, e.g., the pillpod euphorbium, *E. pilulifera*, of India, Australia and tropical countries; *E. xylphylloides* and *E. stenoclada* (rhimba tree), both of Madagascar; and *E. resinifera*, a cactus-like plant of Morocco, the source of the gum euphorbium, used in veterinary practise as a vesicant. Gum euphorbium contains 38 per cent of resin, some calcium malate, much wax, and minor amounts of other substances.

There are also a few waxes of herbs which are possibly worthy of exploitation, such as flax, cotton, hemp, and broom. These waxes are obtainable from the waste by-products of industries engaged in the utilization of natural plant fibers. Attempts have been made in European countries and in South America to recover such waxes economically, and with some measure of success. The only wax of the shrubs and herbs that has entered the American market in large tonnages is candelilla wax.

Candelilla Wax

In 1909 the Journal of the Royal Society of Arts (Vol. 57, p. 64) announced that the wild plant known as candelilla contains wax of excellent

quality and in sufficient amount to make it extremely valuable. The report noted that the plant grows in the following states of Mexico: Tamaulipas, Coahuila, Nuevo Leon, Baja California, Jalisco, Puebla, and San Louis Potosi. To this list of states might be added Durango, Zacatecas, and Chihuahua.

Candelilla wax is obtained from the coating on the succulent plant, *Euphorbia cerifera* Alcocer, or *E. antisyphilitica* Zuccarini. *E. cerifera* is commonly known as the "wax slipper flower" and *E. antisyphilitica* as "wax euphorbia," both related to the spurge family, order *Euphorbiaceae.*

There are also related species of these shrubs, known as *Pedilanthus pavonis* Boissier, and *Pedilanthus aphyllus* Boissier. The latter is commonly known as the "leafless euphorbia," and is not considered as important a source as *P. pavonis.* The common name "jumete" has been given to these *Pedilanthus* species, which are said to yield less wax than the candelilla shrubs of the *Euphorbia* species. Genetically the word *Pedilanthus* is from the Greek meaning "sandal flower," and *pavonis* was named for Josef Pavon, botanical traveller in Peru. The Mexican native speaks of the candelilla weed as "jirba." Members of the spurge family may be distinguished botanically by their three-celled ovaries and lactiferous juice; a reed-like stem is characteristic of *Pedilanthus.* The candelilla grows in arid regions of northern Mexico, southwestern Texas, Arizona, and southern California. The wax obtained from the *Euphorbia* species is rated as the chief economic source, and is of a higher melting point and higher saponification number than the wax obtained from the *Pedilanthus* species. At one time it was thought that the wax of the candelilla had a medicinal value.

Some attempts have been made to cultivate the candelilla in the United States (Texas and Arizona), Haiti, and Santo Domingo, but with little success. The possible cultivation and harvesting techniques of candelilla have been fully discussed by Daugherty and associates[65b] of the Georgia Institute of Technology, in a bulletin entitled "A Survey of Candelilla and Candelilla Wax."

Enormous quantities of candelilla in its wild state are encountered in southwestern Texas. It ordinarily grows 2 to 5 feet high and hundreds of leafless stalks, ¼ inch or thicker, may come from the same root system. The candelilla growth begins at the mouth of the Pecos River and extends to Sierra Blanca, covering all of the counties of Terrell, Brewster, Presidio, and El Paso. Knaggs[128] has described the growth of the plants at Regan's Canyon in the Big Bend country of Brewster County as follows: "Everywhere we looked there was candelilla growing. In the bottom of the gorge, along the slopes of the palisades and hanging on the rock shelves of canyon walls—it was growing in large clumps everywhere but never alone. Five or six hundred light-green stems, measuring 2½ feet tall, sprang from a

central root system—they resembled a bunch of green rat tails standing on end."

There are about six factories in the candelilla-growing country turning out wax, including a large one in San Antonio.

Hare and Bjerregaard[97] in 1910 prepared the wax from bundles of plant stems received from Mexico. The species of plant they believed to be *E. antisyphilitica*. They extracted the wax with boiling water (apparently *without* the addition of sulfuric acid) and obtained a dark, impure cake. They dissolved it in hot chloroform, redissolved it in a mixture (3:2) of ethanol and benzene, filtered hot, and evaporated off the solvent. In this manner a pale grayish opaque solid was obtained. When this was remelted and dried to a moisture-free basis, a brownish-colored wax resulted which could be bleached by exposing it to the sun if it were first formed into a sheet. About 2.5 per cent of wax was obtained from the plants. The wax prepared by Hare and Bjerregaard had a high iodine number and high acid value. If the wax from *E. antisyphilitica* had been acid-treated it would have had a low acid value.

The candelilla industry is said to have been started in the Monterrey and Torreon districts in about the year 1913 by Oscar Pacius. Dickinson[67] has described the production of candelilla wax in the region of Monterrey, where there are four wax refineries. The description is similar to that already given except that in the refining at Monterrey steam is used to melt the crude wax instead of water over a firebox. Dickinson says that yields of 3½ to 5 per cent of the crude wax (ostensibly from *Euphorbia* species) have been reported. Farcy[76] reported a yield of 3 per cent of candelilla wax by boiling out the stems of *P. pavonis*. The yield of wax from *Pedilanthus* species is said to be less than that from *Euphorbia* species.

Extraction of Wax from Plants. The wax can be extracted from the surfaces of all parts of the plant except the root. The general practise, however, is to pull the stalks up by the roots and to extract the whole plant in the producing area. Attempts made at cutting candelilla mechanically did not preserve the root system. Were the plants shipped a great distance to a central refiner, it would be practicable to ship only the more or less reed-like stems. Hare and Bjerregaard[97] had bundles of stems shipped from Mexico to a pilot plant in New Mexico which they established.

Little improvement has been made in the methods used for extraction of the wax of the candelilla plant. Knaggs[123] has described the extraction as it is carried out in a region between Satillo and Parras: "Great heaps of the freshly gathered, light blue-green shrubs lay in high piles in readiness for extraction. Other piles were brown in color, the wax having been removed. The extracted plants were being spread on the ground to dry so that later they could be used for fuel under the cooking tanks. There were

four cooking units. . . . The steel cooking tanks were set flush in the ground and a pit dug under them which served as a firebox. A crude piece of stove pipe extended about three feet above the ground and was connected to the earthern firebox in order to form a draft. Water was charged into the tank and the unit filled with green candelilla plant until it was piled up to about a foot above the sides of the vat. An iron grating which was fastened by hinges to one end of the tank and which covered the entire surface of it, was used to force the candelilla plant down under the surface of the water. . . . When the water came to a boil, a small amount of sulfuric acid was added, to facilitate releasing the wax from the plant, as the wax is only on the surface of the shrub." Eight kg of sulfuric acid is added for each 100 kg of candelilla plants. "After boiling for a sufficient length of time for all the wax to be released and rise to the surface, the fire is allowed to die down and the grating lifted. At this point a worker began skimming the floated wax from the surface of the water. He used a shallow collander-like ladle with a handle attached. As he skimmed the melted wax, most of the water which was picked up in the skimming operation travelled out through the holes in the bottom of the collander and back into the tank, leaving the wax on the surface. The skimmed wax was quickly poured into the bottom of an old fifty-five gallon drum." Daugherty and associates[68b] give a similar description, but state that the dark scum of wax from the cooking tank "is carefully skimmed and transferred to another container in which it is again treated by boiling with sulfuric acid. The wax is then allowed to solidify, the water layer is drawn off from the bottom, and the wax cake removed from the drum. The center layer of the cake is cut out and shipped to refiners. The top and bottom portions, which contain a high percentage of foreign matter, are thrown back into the tank with the next charge . . . . Large-scale operators can operate profitably at a crude yield of about 1.75 per cent."

The region of the candelilla country in the State of Coahuila is so dry that water supply is always a major problem. A considerable amount of dirt from the root of the plant, sand, and plant fragments is mixed with the wax when it floats to the surface in the vat; therefore when the wax cake is lifted from the drum, only a small middle section is cut for sending to the refiner, a large wheel of chalky grayish-white, differing in color from the refined wax. The crude wax also contains much water. A harvester must pull 1000 pounds of shrub to produce 30 pounds of wax.

Refining of Crude Candelilla Wax. Refining of the crude wax is conducted in the larger centers, and not in the field. Knaggs[128] describes the equipment and process used in a typical refinery. A steel cooking tank mounted on a high stone platform, under which is located a firebox, is filled about two-thirds with the chalky grayish-white crude wax. While it is melt-

ing, it is continuously stirred with a long wooden paddle to keep it from scorching and frothing over. Every so often a small amount of sulfuric acid is added. The acid neutralizes the alkaline earth salts, thereby preventing emulsification of the wax. The acid also destroys foreign organic matter, which results in an improvement in color. The cooking goes on for hours. The tank, at Parras, is drained onto a stone floor where the wax is allowed to solidify. It is then broken up into lumps with a sledge hammer and packed into burlap bags to be sent to the trade center which in this instance is Satillo, west of Monterrey.

In southern Texas the stalks are dried for several days and then immersed in hot water held in wooden tanks. Sulfuric acid is added to the water and the wax is then skimmed off the surface, strained, and cast into cooling pans. A second melting in acidulated water follows and the recovered wax is then cast in pans for marketing[146]. The wax yield is about 2 per cent of the weight of the plant.

Refining may be carried further in some instances to produce a so-called "double-refined candelilla wax," or carried out still further to remove practically all of the resinous constituents.

The color of refined candelilla wax is that of *café au lait*. The sole criterion for degree of purity is the color, judged by the comparison with a standard block of wax[68b]. Suggestions have been made from time to time for removing the color-imparting resinous compounds from the wax in the refining. Chromic acid is reported as an effective agent. If the candelilla is to be used in combination with paraffine, these resinous compounds may be removed by simply melting the wax with three parts of paraffine and either allowing the resinous compounds to settle out or hastening their separation by filtration with active chars, fuller's earth, or a mixture of these. Good results are also obtainable by treating the candelilla-paraffine mixtures with hydrogen peroxide and potassium permanganate.

Extraction of Candelilla with Solvents. Daugherty and his associates[68b] have noted that the extraction of candelilla with solvents gives good results, the procedure being varied depending upon the solvent used. "The principle, however, is always the same. The hot solvent vapors are kept in continuous contact with the wax-bearing material and allowed to condense, carrying the wax away from the plant material. The process is continued until no color is detected in the condensing solvent, indicating that no more wax is being extracted. The wax obtained by this method contains considerable resin, which is separated by means of a centrifugal apparatus and extracted from the wax with alcohol. Solvent extraction should be less costly and should result in higher yields of wax recovery; however, the large initial outlay for equipment and the previously mentioned dispersed areas of growth of candelilla have hindered the progress of utilizing this method"[68b].

"Durango wax" is the name given to a candelilla derivative marketed by Candelilla Industrializada, S.A. (Mexico). Its melting point is 75–76°C, and iodine number 9. The wax is said to be obtained by extracting the resins out of double-refined candelilla wax. It is not unlike that obtainable from *E. antisyphilitica*. Because Durango wax is resin-free it is particularly desirable for use in polish and carbon paper manufacture.

Practically all known commercial production of candelilla wax originates in six states of Mexico, and the product is distributed through an organization designed to sell collectively all the wax produced. This organization functions under the sanction of the Banco Nacional de Comercio Exterior, through which the sales are made.

Properties of Candelilla Wax. Candelilla wax of commerce is marketed in opaque lumps that are brownish or yellow-brown in color, hard, brittle, and easily pulverized. Its surface is capable of taking a high polish, and it is this property which imparts a luster to polishes. Candelilla wax has the odor of beeswax when warmed, and burns with a bright flame. It is only soluble in cold ether to the extent of 0.12 gram in 100 ml, and even less soluble in ethanol. It is sparingly soluble in cold chloroform, turpentine, petroleum spirits, or acetone. It is readily soluble in all of these solvents hot. About 4 to 5 grams of candelilla wax dissolve in 100 grams of turpentine or turpentine substitute at 25°C, and the same amount in pine oil at 35°C. A mixture of 3 parts of absolute alcohol and 2 parts of benzene (90 per cent) makes an excellent hot solvent.

Alcocer and Sanders[3] reported that the Mexican plant yielded 2½ to 5 per cent of wax on the dry plant basis, and that the physical and chemical constants vary with the age of the plant and the year in which it is collected. Plants grown on the coast contain less wax and more caoutchouc latex than those grown in the interior. These investigators reported the following constants for wax prepared from the plant stems of *Euphorbia cerifers*: density (d_{15}^{15}) 0.9820–0.9856; refractive index (n_D^{35}) 1.4545–1.4626; acid value 12.73–18.11; saponification number 35.0–86.5; R−M number 0.53–7.69; iodine number 14.42–20.40; nonsaponifiable 76.70–77.27 per cent; hydrocarbons 42.49–59.70 per cent. Densities (d^{15}) reported by several investigators have ranged from 0.936 to 0.993, Hare and Bjerregaard[97] reported the refractive index ($n_D^{71.6}$) of crude candelilla (*E. antisyphilitica*) wax as 1.4555.

The physical and chemical constants of candelilla wax as derived from various sources have been determined by Hare[97], Lüdecke[103], Sanders[239], and Deiler[83]. Farcy[75] has published constants on the Mexican variety, *P. aphyllus*, which apparently contains a lesser amount of hydrocarbons (33 per cent) than *P. pavonis* which has 49 to 54 per cent. The hydrocarbons are believed be C_{29}, C_{31}, and C_{33} normal paraffins. The constants are:

TABLE 40

CONSTANTS REPORTED FOR CRUDE CANDELILLA WAX

	Hare[95]	Schuette[247]	Findley[79]
Acid value	12.4	19.0	20.2
Sapon. number	64.9	49.0	56.7
Iodine number	36.8	32.8	27.9
Melting point	67–68°C	69–71°C	60–72°C

CONSTANTS REPORTED FOR REFINED CANDELILLA WAX (*Pedilanthus* spp.)

	Lüdecke[139]	Sanders[199]	Deiler[82]	Leys[141]	Findley[79]
Acid value	8.9–19.0	14.4	19.0	19.4	20.2
Sapon. number	54.0–61.4	46.7	59.7	53.5	49.9
Iodine number	13.0–22.9	16.6	14.0	12.9	23.1
Melting point	68.7°C	67.5°C	66°C	71°C	60–73°C

CONSTANTS REPORTED FOR CANDELILLA WAX (*E. antisyphilitica*)

	Olsson-Seffer[202]	Sanders[199]	Anon.
Acidity (%)	0.32	0.03	—
Sapon. number	104–108	105–106	105–106
Iodine number	5.23	5–6	5.2–5.55
Density (d^{15})	0.9473	0.9587	0.9470
Melting point	77.4°C	74–80°C	75.8–77.4°C

density (d^{15}) 1.001–1.002; melting point 64–65°C; acid value 18–19; saponification number 66–67; iodine number 20–21.

At the Tezonpa Botanical Station, Olsson-Seffer and Sanders[202] examined the wax of *E. antisyphilitica* which apparently differs a little from *P. pavonis*, and found it less resinous, and lower in both acid value and iodine number. The wax also had a higher melting point.

Ulmann[288] gives the following analytical constants for commercially refined candelilla wax: specific gravity (d^{15}) 0.982–0.996; melting point 66–70°C; acid value 12.7–18.5; saponification number 56.3–63; iodine number 13–25.5; unsaponifiable 66–74 per cent.

Hare and Bjerregaard[97] give the specific gravity (d_{15}^{15}) of the crude wax as 0.9825. Deiler[82] gives the specific gravity (d_{15}^{100}) as 0.877 for the wax when melted. The mean value of the melting point is 67.4°C, and solidifying point 64.5°C. Buchner[41] determined the acid value as 16.96, Hare and Bjerregaard as 17.4 (on sample rendered ash-free), and Findley and Brown[79] as 20.2. Buchner[41] determined the ester value as 33.86, and Findley and Brown as 36.47. Zöllner[332] gives the saponification number of candelilla wax as 59.4–60.1 when determined by the Hezel method (diethylene glycol as solvent), vs. 54.8–55.4 by the International Commission method. Findley and Brown[79] report a lower iodine number for refined than for crude candelilla wax, namely 23.1 vs. 27.9. They also report a hydroxyl value of 15.7 for refined vs. 23.0 for the crude wax, and a mean molecular weight of 510.2 for refined vs. 531.9 for the crude.

TABLE 41. DIFFERENCES IN CONSTANTS OF REFINED WAXES DERIVED FROM SEVERAL SPECIES OF CANDELILLA

	E. cerifera	*E. antisphyliciata*	*P. pavonis*
Melting point (°C)	67–79	68–80, 77.4[a]	66[b]–73
Setting point (°C)	63–68[b]	63.8–67.7	63–68[d]
Saponification number	35.0[b]–86.5[a]	104–108[a], 84.1	46–52, 49.9[e]
Iodine number	14.4–27.2[a]	5–6[f], 33.6[e]	12–22.9, 23.1[g]
Acid value	12.7–18.1[a]	12.4–17.4[e]	8.9–19.4, 20.2[g]
Density at 15°C	0.9820–0.9856[a]	0.9473[a]–0.9920, 0.9825[e]	0.950–0.993
Density at 100°C	—	0.8850	0.8700[b]
Refractive index at 71°C	—	1.4555[e]	—
Refractive index at 85°C	1.4545–1.4626	—	1.4555–1.4560[d]
Nonsaponifiables (%)	67.5[b]–76.7[f]	84.2[e]	65–76.7
Hydrocarbons (%)	42.5–59.7[a]	57[g]	48.6[b]–54.3
Ash content (%)	0.7[b]	0.34[e]	0.05
Moisture content (%)	0.52–1.5	—	0.74
Dielectric constant	—	—	2.50–2.67
Acidity (%)	0.003	0.03–0.32[e]	—

[a]Alcocer and Sander (1910); [b]Deiler (1909); [c]Hare and Bjerregaard (1910); [d]Hilditch (1945); [e]Olsson-Seffer (1910); [f]Sanders (1912); [g]Findley (1953); [h]species of source not specified but classed as *E. cerifera*; Garcia Cruz (1939); J. Berg (1915).

Chemical Composition of Candelilla Wax. Investigators have differed in the amount of unsaponifiables which may be obtained from candelilla wax. This disagreement in their reports may be chiefly due to the difficulty encountered in fully saponifying the wax. For example, the figure of 67.5 per cent unsaponifiable obtained by Berg[24] would seem too low. On the other hand there is a fairly close agreement as to the amount of hydrocarbons, whether obtained by older methods or the newer ones of chromatographic procedure and x-ray analysis. In 1912 Alcocer and Sanders[2] had reported a mean of 50.01 per cent of paraffin hydrocarbons. In 1914 Berg[24] reported 50.0 per cent of paraffins; Buchner in 1918 reported 50–52 per cent; Leys[161] in 1925 reported 54.3 per cent on an ash-free basis, and more recently in 1949 Schuette and Baldinus[246] reported 52.2 per cent of *n*-paraffins. Alcocer and Sanders[2] found that extreme variations in hydrocarbons content can occur in accordance with the age of the plant and season of growth; namely 42.49 to 59.7 per cent. The average paraffins content of commercial candelilla wax of known purity may be regarded as 51.5 per cent.

The paraffins consist of C_{29}, C_{31}, and C_{33} hydrocarbons. Sanders[239] determined the chemical characteristics of a sample of wax which had been prepared from candelilla plants collected in the month of January in Coahulia, Mexico. The wax was of a greenish-white appearance and had a granular fracture. The dry wax yielded 77 per cent of unsaponifiable matter, and contained 48.6 per cent of paraffins. The chief constituent of the unsaponi-

fiable proved to be *hentriacontane*. *Myricyl alcohol* was also identified as a constituent. Meyer and Soyka[190] extracted candelilla wax with 96 per cent alcohol, and obtained 18 to 20 per cent resinous matter. The resin-free wax was extracted with hot ethanol which removed 74–76 per cent of material which they considered to contain a hydrocarbon (m. 71°C, b_{15} 310°C) higher than the C_{31} hydrocarbon.

Fraps and Rather[82] in 1910 extracted dry saponified candelilla wax with ether for 40 hours, and obtained 40 per cent of extractive, which when recrystallized from ether gave a batch of white crystals (m. 68°C) identified as *hentriacontane*. Crystals of the latter are readily soluble in hot ether, fairly soluble cold; insoluble in cold alcohol, but slightly soluble hot. The hydrocarbons contained 85.45–85.16 per cent carbon, and 14.10–14.28 per cent hydrogen. A resinous solid accompanying the hydrocarbon in small amount was brittle when dry and melted at 55°C. In 1934 Chibnall and coworkers[49] reported C_{31} and C_{33} *n*- paraffins.

More recently Schuette and Baldinus[246] developed a simple, rapid chromatographic procedure of extracting the hydrocarbons, thus eliminating the involved treatment of saponification of the wax to separate its constituents. The wax was dissolved in dry petroleum ether with the aid of heat and the solution was drawn rapidly by the aid of a slight suction through a long column (14 in. l, 2 in. dia.) of activated alumina. A yellow band denoted the adsorption of the paraffins, which were later removed by washing with petroleum ether, and a white residue of paraffins was obtained upon the evaporation of the solvent. The residue after purification with acid (H_2SO_4) and recrystallization with petroleum ether yielded a crop of beautiful white crystals. To separate the hydrocarbons the Hirschler and Amon[107] technique of adsorption with silica gel of the wax was followed. After many days the solution-percolate from the 65-in.-long tube began to drip from the bottom, and the fractions removed were evaporated and recrystallized from benzene, and subjected to x-ray analysis. These fractions showed long spacings of 41.4, 42.2, and 41.7 Å, with solidification points of 66.1°, 67.7°, and 67.4°C. From the data on long spacing, solidification point, melting point, and first transition point on heating, of both the candelilla and the synthetic hydrocarbons used as a comparate, the proportion of different hydrocarbons could be estimated. The hydrocarbons, *n*- paraffins, consist of 90 per cent *hentriacontane*, and 5 per cent each of *tritriacontane*, and *nonacosane*. The latter C_{29} *n*- paraffin was reported for the first time as a constituent of candelilla wax. No ketones were found in the unsaponifiable.

Meyer and Soyka[190], after extracting the resin from candelilla wax with ethanol, distilled the resin with zinc and obtained a colorless oil (b. 223–245°C), which had the properties of a sesquiterpene. They removed the hydrocarbons from the resin-free wax by extracting them with hot ethanol,

and there remained 5–6 per cent of a residue (m. 88°C) which they considered to be a *hydroxy lactone*, $C_{30}H_{58}O_3$. The latter reacted neutral, was stable to $KmNO_4$ in alcoholic solution, and bore a similarity to an OH-lactone found in wool wax. The lactone had a molecular weight of 466.78 and an ester number of 120. Schuette and Baldinus[246] were unable to isolate a lactone from candelilla wax, and state positively that none is present.

In 1914 Berg[24] found that candelilla wax contained nonsterolic esters of 88–90°C melting point, also a small amount of high molecular weight non-acetylizable substance soluble in alcohol, which melted at 243°C with decomposition. He reported the wax to contain 50 per cent of hydrocarbons, one of which melted at 68°C and the other at 84–85°C; and also 10 per cent of a clear half-liquid mixture of two sterols. The presence of a hydrocarbon of 84–85°C melting point has not been confirmed. The nonacetylizable substance might possibly be *β-amyrin acetate* (m. 240.5°C) and the substance with 84–85°C melting point *myricyl alcohol* (m. 86.5°C).

Sanders[229] in 1911 had noted the preponderance of a C_{30} alcohol (m. 86–88°C) in the wax esters, and Chibnall and Piper in 1931 postulated the presence of C_{30}, C_{32} and C_{34} alcohols. Schuette and Baldinus[246] have reported a normal C_{28} acid in addition to the normal C_{20}, C_{32} and C_{34} wax acids reported by Chibnall and Piper, as a result of their x-ray and melting point determinations. One sterol has been identified as a phytosterol, namely *sitosterol*.

The composition of unhydrolysed crude candelilla wax has been calculated by Findley and Brown[79] by using functional group analysis and fractionation by molecular distillation. They give the following mols per cent of constituents for crude candelilla: hydrocarbons 46; free alcohols 13; free acids 7; simple esters 2; hydroxy esters 8; acid esters 10; and diesters 9. They also give the following mols per cent of constituents for refined candelilla: hydrocarbons 57; free alcohols 14; free acids 7; simple esters 21; hydroxy esters 8; acid esters 0; and diesters 0. These investigators report that 48 per cent of the fatty acids of crude candelilla wax are hydroxy acids, whereas those of refined candelilla are 17 per cent.

Density and Coefficient of Expansion: The density (d^{15}) of a specimen of candelilla wax as received from the refinery was 0.9956. Upon melting and slowly resolidifying the density decreased to 0.9846[211a]. The great difference in density between the lump candelilla and the cake of remelted wax is difficult to explain on the basis of differences in the rate of cooling. Such behavior is not uncommon with solvent-extracted waxes.

The density increments at 25°C are 0.00047 and 0.00039 for the "original" and "resolidified" waxes. Above 50°C candelilla wax expands rapidly with increasing applied heat until it begins to flow. In the molten state the expansion is less rapid, as the density decreases 0.00051 per temperature

TABLE 42. THE APPROXIMATE COMPOSITION OF COMMERCIAL REFINED CANDELILLA WAX

Hydrocarbons: (m. 68°C)	50–51%
Nonacosane (2.5%)	
Hentriacontane (46–46.5%)	
Tritriacontane (2.5%)	
Esters of Wax Acids and Alcohols: (m. 88–90°C)	28–29%
Simple esters (and lactones?) (20–21%)	
Hydroxylated esters (6–8%)*	
Free Alcohols, Sterols and Neutral Resins:	12–14%
Myricyl alcohol (m. 84–85°C)?	
Sterols (sitosterol, etc.) (7–8%)	
Resins (as β-amyrin acetate) (5–6%)	
Free Acids:	7–9%
Straight chain (m. 69°C): wax acids (6–7%, H & B)	
Cyclic: resin acids	
Mineral Matter:	0.7%
Volatile Matter:	0.5–1.0%

* The ester of sitosterol ($C_{29}H_{49}OH$) and dihydroxymyricinoleic acid ($C_{30}H_{62}O_4$ constitutes about 20 per cent of the ester portion of the wax. Also present are esters of the normal acids and alcohols—C_{28}, C_{30}, C_{32}, and C_{34}. Some free acids are present as well as amounts of the above acids (Daugherty *et al.*, 1953)[68b].

TABLE 43. DENSITIES OF COMMERCIAL CANDELILLA WAX (M.P. 70.5°C)

In Lumps from Refinery	After Remelting and Casting in Tin
27.8°/15°C 0.9911	26.7°/15°C 0.9803
44.4°/15° 0.9823	39.7°/15° 0.9752
	47.2°/15° 0.7723

	Density			
	at 25/15°C	at 35°/15°C	at 77°/15°C	at 100°/15°
Original (as received)	0.9919	0.9874	0.8670	0.8550
Remelt (slowly congealed)	0.9809	0.9770	—	—

Note: Densities at 25° and 35° are computed, those at 77° and 100° on molten wax were determined by means of a Westphal balance.

degree. This behavior is not uncommon to that of waxes in general, but is particularly like that of the harder waxes such as carnauba and ouricuri.

The volume decrease of candelilla wax during solidification and crystallization is 12.4 per cent for the "original," and 11.5 per cent for the same wax "remelted and recast." Candelilla wax has a mean cubical expansion coefficient of 0.000404 at 25°; and 0.000608 at 100°C. The only waxes with a lower coefficient are carnauba and ouricuri, all determinations being made on specimens remelted and solidified in the air with slow cooling.

Wax Blend of Candelilla and Paraffin Wax. The dry melting points for various blends that have been made with paraffine and candelilla wax (128°/130°F m.p.) are given in Table 44.

TABLE 44. DRY MELTING POINTS OF PARAFFINE—CANDELILLA WAX BLENDS

Per Cent Candelilla	Melting Point °C	Melting Point °F
0	54.0	129.2
5	55.0	131.0
10	58.0	136.4
20	60.4	140.8
30	61.2*	142.3*
40	61.5	142.7
50	62.6*	144.7*
60	63.4	146.1
70	63.7*	146.8*
80	64.6	148.3
90	66.6*	152.0*
100	70.5	159.0

* Computed from plotted curve.

It will be noted that the addition of 20 parts of candelilla wax to 80 parts of paraffin increases the melting point of paraffin, but there is little further increase when the candelilla constitutes 20 to 80 per cent of the blended wax. In this range the hardness of paraffin is substantially increased without much of an elevation in melting point. Further additions of candelilla to paraffin greatly increase the melting point, but are not required to increase the hardness of the blended wax.

It will be observed that the addition of candelilla wax to paraffin in proportions greater than 5:95 increases the hardness of the paraffin to a pronounced degree; also that candelilla wax retains its hardness even if there is 20 per cent of added paraffin in its composition.

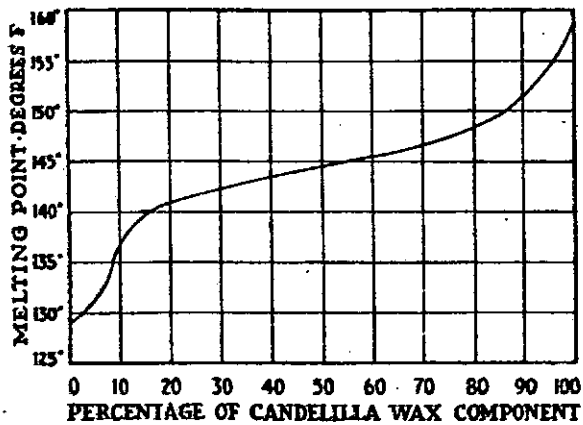


FIGURE 6. Graph showing increase in melting point of paraffine by addition of candelilla wax.

TABLE 45. HARDNESS OF PARAFFINE—CANDELILLA WAX BLENDS
(Paraffin of 54°C, and Candelilla Wax of 70.5°C M.P.)

Per Cent Candelilla	Durometer (Shore units at 86°F)
0	70
5	70
10	80
20	84
40	94
60	98
80	100
100	100

Uses of Candelilla Wax. Candelilla wax is used extensively as a luster-producing hard wax constituent in polishes of all kinds. It is often used in conjunction with carnauba wax, which latter is somewhat superior in both hardness and luster-producing power. Candelilla is used quite extensively to harden other waxes, particularly in hardening them without greatly increasing the melting point. Candelilla wax is used as an ingredient in leather dressings, shoe stains, liquid polishes for wood, floor waxes, shoe pastes, sound records, electrical insulators, candle compositions, sealing wax, and in the manufacture of celluloid, rubber compositions, paint remover, linoleum, and waterproof boxes and fabrics. It is used in chewing gum.

As a finishing material in the textile industry, candelilla wax can be effectively used with japanwax or with rosin in emulsion recipes (Herbig[103]). Examples are: pale candelilla 4000, rosin 1000, potassium hydroxide 0.5, sodium hydroxide 50, and water 28,000 parts by weight; pale candelilla 25,000, japanwax 2500, potassium hydroxide 0.5, sodium hydroxide 50, and water 30,000 parts.

Candelilla wax is offered on the market as crude (in bags), refined (in bags), and powdered (20 mesh, 80 mesh, and 100–200 mesh) form. The nominal prices for November 1950 were 60 to 62 cents per pound for *crude*, 65 to 68 for *refined*, and 5, 5½, or 6 cents extra for *powdered* depending upon the fineness of mesh. Quotations for candelilla wax contrast with those for ouricury wax (85 to 86 cents), and carnauba wax (97 to 98 cents).

The U.S. importations of candelilla wax increased from 900 to 2822 short tons in the period of 1936 to 1941. In 1943 importations reached 5440 tons, but declined to 1297 tons in 1948. Since then the annual imports have averaged 2850 tons valued at $2,750,000. The unit value was only 12½ cents per pound in 1939, but rose to 70 cents per pound in 1952.

Retamo Wax. Wax is obtained from a species of plant known as *Bulnesia retama*, which is a shrub or small tree (3–5 ft) native to Argentina. The wax is found on the branches of this plant which grows in arid lands at the foot of the Andes Cordillara mountains. The branches are generally harvested in summer, dried to loosen the wax from the cellulosic material, and

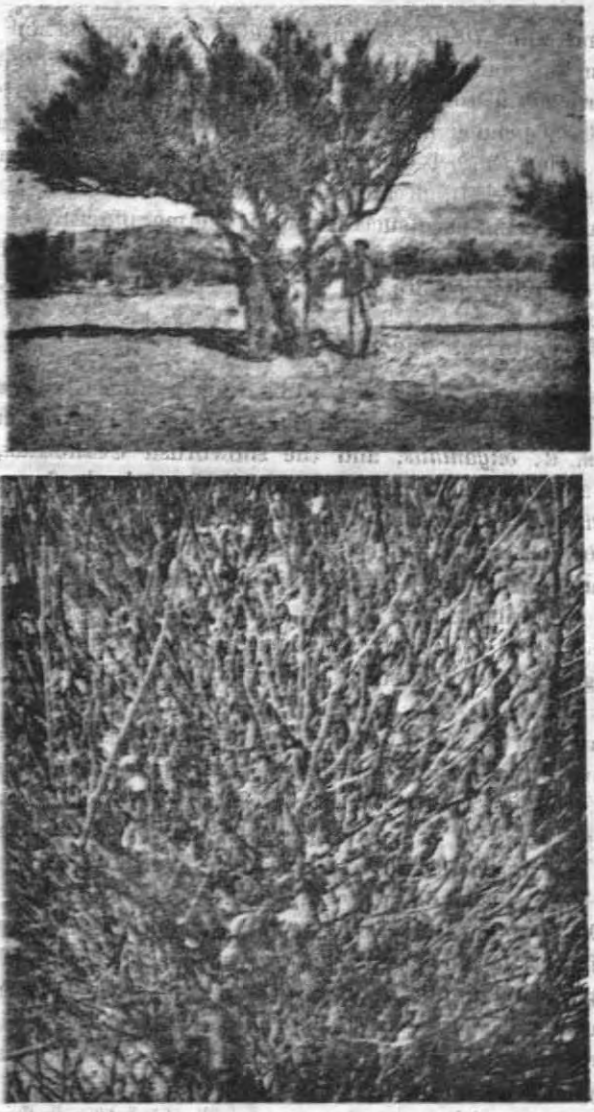


FIGURE 7. A *Bulnesia retama* tree at Campo Punta del Agua, province of San Juan. Bottom: Shrub or small tree, showing small flowers which bloom on the branches in the spring (lower slopes of the Andes Cordillera, Argentina). *Bottom photo courtesy of A. Gentilhomme, Productos Químicos y Vegetales, Buenos Aires.*

then boiled in water acidified with sulfuric acid to readily free the wax. Processors of the wax is the Productos Químicos y Vegetales, S.A.I.C., of Buenos Aires.

The characteristics of Retamo wax as given by the aforesaid company

are: melting point 76–78°C, acid value 48.6, saponification number 87.3, ester value 38.7, iodine number 4.5–5, acetyl number 17, hydrocarbon content 27 per cent, acetone soluble 2.5–3 per cent, ash 0.03 per cent, moisture 1 per cent, suspended matter 0.14 per cent, isopropanol insoluble none, refractive index (n_D^{65}) 1.448. The wax is a hard wax (penetration 100 g/75°F/5 sec, 0.5–1.0), of café au lait color, and odorless.

This wax is being used successfully in the manufacture of shoe polishes, floor polishes, automobile polishes, in certain tannery finishes, edge inks for shoes, carbon paper, etc.

Waxes of *Ceanothus* Species

Various species of *Ceanothus* shrubs, family order Rhamnaceae, are wax bearing, for example the hoaryleaf Ceanothus, *C. crassifolius*, the hairy Ceanothus, *C. oliganthus*, and the snowbrush Ceanothus, *C. velutinus* Douglas, also known as "tobaccobrush" since the leaf was used by the Indians instead of tobacco.

The snowbrush is a widely branching shrub two to six feet in height, and its habitat is bounded roughly by the Coast Range of California on the west, the Columbia River on the north, Colorado on the east and San Francisco Bay on the south. It is plentiful in the Shasta National Forest in the neighborhood of Sisson, California. The brush is rich in tannin (17.3 per cent) and wax.

The leaves of the dried brush can be ground, sifted, and extracted with gasoline or other suitable solvent. Scalione and Blakemore[241] obtained a wax yield of 7.3 per cent from old foliage of *C. velutinus*. The wax has a darkish olive-green color, is hard and brittle, and breaks with a conchoidal fracture. The characteristics of a specimen of wax were as follows: melting point 78–79°C; specific gravity (d_{15}^{15}) 0.988; acid value 20.3; saponification number 93.4; iodine number 19.3; and Reichert-Meissl number 7.5. The unsaponifiable matter contained hydrocarbons (m. 50 to 57°C).

The high R-M number indicates the presence of an appreciable amount of soluble fatty acids over and above that associated with glycerides, of which these investigators found only a trace. The commonest of the R-M acids in plants is *isovaleric*, which is customarily found in the combined state as an ester with a sterol or terpeneol; the latter is fairly common to plants possessing more or less resinous waxes.

The wax of *C. velutinus* according to Scalione and Blakemore[241] contains *ceryl* and *myricyl alcohols*, *palmitic*, *stearic*, and *cerotic acids* (latter in free state), hydrocarbons, and resins. Assuming that the resinous constituents include α or *β-amyrin* (inclusive of derivatives) and *ursolic acid* as the principal free acid, the approximate composition of the wax would be as given in Table 46.

TABLE 46

Alkyl Esters of Fatty Acids:	55–58%
Ceryl palmitate	
Ceryl stearate (small amount)	
Myricyl palmitate	
Steroids:	20–21%
Phytosterol	
α or β amyrin isovalerate	
Free Acids:	16–17%
Ursolic acid	
Resin acid	
Palmitic acid	
Cerotic acid (small amount)	
Hydrocarbons:	4–7%
Hentriacontane	

Scalione and Blakemore stated that the shrub is so rich in wax that it is a fire menace in the California forests. It appears that over 100,000 tons of the brush are available in the Sisson district alone; sufficient to produce 5000 tons of wax for the market. Along with the wax it would be possible to furnish an enormous amount of catechol tannin which with a plumping agent can be used for the tanning of hides.

In 1942 Metcalfe of the California Forest and Range Experiment Station, at Berkeley, California, recovered residual waxes from *C. oliganthus* and *C. crassifolius*, when distilling the foliage material of these shrubs with xylene in order to obtain the water content of both old and new foliages of these plants.

The foliage of the hoaryleaf Ceanothus, *C. crassifolius*, yields a dark olive-green wax of great hardness and of very high melting point. When semi-refined by boiling it with sodium carbonate solution it loses 6.5 per cent in weight, but is not then blendable with paraffin wax. After treatment with fuller's earth the crude wax is dark yellow in color. McBeth and Warth[154a] have determined the analytical constants of *C. crassifolius* wax as acid value 89, saponification number 140.5, iodine number 31.7, and unsaponifiable 32.1 per cent. The acid value increases with the age of the foliage, from 59.1 to 89.0, and the iodine number from 18.2 to 51.7, the lower values being given by the green foliage. It is believed that the difference is due to the formation of a considerable amount of oleanolic acid acetate in the leaf as it matures and ages.

The resins (sesquiterpenes) have a pronounced terpenic odor which also pervades the unsaponifiable to a lesser extent; they are brown in color, and melt at 235°C maximum, indicating that they are oxygenated. When the resins are removed, the melting point of the crude wax is lowered from 209 to 195°C. Further refinement with fuller's earth brings the melting point down to 178°C. The unsaponifiable is a translucent yellow brittle solid

which melts at 110°C. It is apparently a mixture of *myricyl alcohol*, *amyrenol*, and a small amount of *carotenoids* and *aliphatic hydrocarbons*.

The saponified acids when liberated with strong HCl yielded a brown brittle material (m. 169°C) and white needle crystals (m. 290°C) of *oleanolic acid*. Oleanolic acid occurs in the wax as acetate, thus giving the wax a high ester value. The chemical composition of *C. crassifolius* wax from mature leaves is of the following order: *resin acids* 7.5, *oleanolic acid acetate* 28.0, *cerotic acid* 24.0, *amyrin acetate* 12.5, *aliphatic esters* (as *myricyl palmitate*) 26.0, *carotenoids* 0.8 to 1.2, and *hydrocarbons* 1 per cent.

The Fisher-Johns melting point (bulk) for the crude wax of the new foliage is 214.5°C, and that of the wax of the old foliage 209°C. The physical properties of the wax are enhanced by the addition of ordinary paraffin wax. A wax blend of 4 parts of paraffin to 1 part of Ceanothus wax had a durometer hardness of 93.7 at 25°C. The addition of Ceanothus wax to paraffin elevates both the hardness and the melting point of the latter.

The foliage of the hairy Ceanothus, *C. oliganthus*, yields a soft, dark-colored wax.

Wax of Manzanita Leaves

The bigberry manzanita, *Arctostaphylos glauca*, of the manzanita family of which there are nearly fifty well known species contains a very hard wax on its glaucus foliage. The Fisher-Johns melting point of the wax is 76°C minimum, 205°C bulk, and 230°C maximum. The wax has a neutralization value of 58.8, and an iodine number (Hübl) of 19.0. One of the principal constituents of the wax is *ursolic acid* which is present in large amount and is responsible for its high melting point.

Wax of Scrub Oak Leaves

A residual wax was recovered by the California Forest and Range Experiment Station when distilling with xylene the foliage of the California scrub oak, *Quercus dumosa*. It is a greenish-colored resinous wax of considerable hardness. The Fisher-Johns melting point as determined by McBeth and Warth is 74°C minimum, 174°C bulk, and 178°C maximum. It has an acid value of 59.6, and a saponification number of 123.4.

Wax of Rimu Wood (New Zealand)

Rimu sawdust, a by-product of the rimu dacrydium, *Dacrydium cupressinum*, when extracted with alcohol yields 0.7 per cent of an ether-soluble neutral resin. The resin when distilled yields ferruginol, β-sitosterols, totarol (a sesquiterpene), and a saturated wax (m. 63–64°C) which has the composition $C_{24}H_{48}O_2$, or $C_{25}H_{50}O_2$.

Flax Wax

The outer epidermal layer of the flax stem, *Linum usitatissimum* L., is rich in wax which remains on the fiber through the retting and scutching operations, in the preparation of the bast fibers for the making of linen. The dust falling off during the combing of flax grown in southern Europe contains up to 6 per cent of wax which is of considerable value. The air-dried cortical tissue separated from the flax fiber contains about 10 per cent of wax; the spun fiber 1 to 2 per cent removable by organic solvents.

Flax and its waste products, according to Chilikin[52], contain up to 2.5 per cent of waxlike substances, extractable by benzene; these substances increase to 8.7–13.7 per cent in flax dust. Gibson[87] states that the extraction of compressed blocks of dust leaves a material usable in the manufacture of insulating board. A plant might be profitably operated if it were set up to extract the wax from 100 tons of dust yearly, but it would be more satisfactory for mills to supply dust to a central plant capable of extracting 1000 tons a year.

Higgins[104] studied the behavior of the waxes in the bleaching of textile fibers. He extracted brown linen yarn with various solvents applied in the order of the results given below: ether 1.39, benzene 0.29, ethanol 0.49, hot water 2.03, boiling ammonia 3.27, boiling caustic under pressure 14.00, and hydrochloric acid 0.33. The waxy material removed by the first three solvents contained 27.8 per cent of saponifiable matter; but if the extraction was preceded by lime boiling and souring, 40.0 per cent of saponifiable matter was obtained. Water-retted flax yields 0.7 per cent more wax than dew-retted. Ether extractions increase the tensile strength of the yarn. Lime-boiled and soured, as well as acid-treated, linen yields more wax to ether or benzene than untreated linen.

Flax wax is a hard wax which is quite brittle. The crude wax is more or less dark green in color. When the wax is semirefined it is brown, and dark yellow when more fully refined. Hilditch[105] has given the following analytical constants for the semicrude wax: specific gravity (d_{15}^{15}) 0.908; melting point 61–70°C; saponification number 100–150; saponification equivalent 375–360; iodine absorption number 9–17; free fatty acids (acid value 24–46) computed as oleic acid 12–28 per cent. The wax obtained directly from the air-dried cortical tissue separated from the flax fiber has the following characteristics: specific gravity (d_{15}^{15}) 0.963–0.985; melting point 67.3–69.8°C; saponification number 77.5–83.7; iodine number 21.6–28.8; acid value 17.5–23.8.

Irish flax is reported to yield a wax having 70 per cent of unsaponifiable inclusive of wax alcohols; 28.2 per cent of fatty and wax acids; Reichert-Meissl number 3.2; and ash 0.62 per cent. The wax after being subjected to

superheated steam distillation has a saponification number of 70.2, acid value 33.0, and iodine number 18.0.

The bleaching of linen yarn removes the waxes, as the treatment involves the use of soda ash and lime. Hoffmeister[108] reported that the wax extracted by ether or benzin from flax threads and deposited from these solvents in grains of an indistinct crystalline structure had a melting point of 61.5°C, and a specific gravity (d^{15}) of 0.9083. He stated that the wax can easily be obtained from "flax dust" of the spinning house, of which it forms about 10 per cent. He gave the following chemical constants for the wax: acid value 54.49, saponification number 101.51, ester value 49.54, R-M number 9.27, iodine number 9.61, and Hehner number 98.31.

Chilikin and Kamolova[52] in 1938 reported the following constants for wax-like substances of flax and its waste products: acid value 48.3, saponification number 101.2, iodine number (Hübl) 26.4, acetyl number (Benedict-Ulzer) 20.29, and unsaponifiable substance 80.3 per cent, which is mainly hydrocarbons. Although the acid and saponification values agree well with those of Hoffmeister determined in 1903, the iodine number is considerably higher.

The chemical composition of flax wax appears to comprise *myricyl palmitate, ceryl cerotate, phytosterol palmitate,* and hydrocarbons, *nonacosane* and *hentriacontane*. Hoffmeister[108] described a constituent of the nonhydrolyzable portion as a paraffine-like ceresin (m. 68°C, sp. gr. (d^{10}) 0.9941), which corresponds to hentriacontane. Chilikin and Kamolova[52] reported a hydrocarbon (m. 62°C) in the unsaponifiable, corresponding to nonacosane. Both investigators reported palmitic acid as one of the chief acid constituents, and only a small amount of stearic acid. Chilikin and Kamolova reported the presence of a small amount of linoleic acid. These investigators isolated three wax alcohols—ceryl alcohol, myricyl alcohol, and a branched-chain alcohol which they termed *neoceryl alcohol*. Hoffmeister reported that the acetyl derivatives revealed the presence of phytosterol and ceryl alcohol.

Flax wax will take on a high luster, and thus makes a suitable ingredient for shoe polishes, both liquid and paste. Its use as a general substitute for beeswax has been proposed, since it has a somewhat similar chemical composition. Flax wax can be chlorinated to the extent of 36 per cent, but the chlorinated wax is not stable at boiling water temperature. Cotton fabric treated with chlorinated flax wax was weakened because of the liberation of traces of hydrochloric acid.

Cotton Wax

Raw cotton fiber, *Gossypium* sp., contains about 4 per cent of oil, wax, and resin. The actual wax content is less than 1 per cent. Because of the

waxy and oily substances raw cotton and unbleached cotton yarns and cloth are difficult to wet through with water. The wax was first isolated in a pure state by Edward Schunck, of Manchester, who in 1868 was investigating the nature of the substances other than cellulose contained in unbleached cotton yarn; the impurities constituted somewhat less than 0.5 per cent. Schunck boiled the cotton yarn in a kier with soda ash, and acidulated the kier liquor with sulfuric acid. From the precipitate he isolated cotton wax, fatty acid, pectic acid, coloring matters, and albuminous substances. The wax had a melting point of 85.5°C (186°F), and the white solid fatty acid melted at 55.5°C (132°F). The yield of wax extracted by this crude method was only 0.004 per cent, and the natural wax was undoubtedly altered by the prolonged boiling in alkali.

In subsequent years benzene extractions of cotton fiber were reported with yields of 0.09 to 0.53 per cent of the waxy constituents. In 1911 Knecht and Allan[130] extracted cotton lint with petrolic ether and then with benzene; they used a Soxhlet apparatus, and obtained two fractions of wax. The first fraction they described as an odorless, dull yellow substance closely resembling beeswax in texture and fracture. The fraction of wax obtained from the benzene extraction was a dark green granular mass (m. 68°C). By repeated treatment of the petrolic ether extracted-wax with boiling ethanol (96%) they obtained 18.8 per cent of a residue which consisted of an insoluble glass-like wax which has a melting point of 79°C (174°F), and has an iodine number of 11.3. The portion soluble in ethanol was more plastic and melted at 62°C (143.6°F), and had an iodine number of 33.4. The Knecht-Allan separation of the components of the glassy wax will be referred to later.

In 1912 Knecht[129] extracted raw Egyptian cotton-sliver (commonly known as Levant cotton, *G. herbaceum* L.) exhaustively with benzene, and obtained 0.47 per cent of a crude cotton wax resembling beeswax. On treatment with petrolic ether the crude wax could be resolved into two constituents: (1) "soluble cotton wax A" (70%) which proved to be a true wax (m. 66–67°C) of pale color, and which contains some free fatty acids, very little glycerides, and some hydrocarbons; (2) "insoluble cotton wax B" (30%), a dark green plastic substance (m. 68°C) containing very little free fatty acid. Texas cotton yielded 0.55 per cent of the crude wax. Bengal cotton, *G. arboreum* L., commonly known as Asiatic tree cotton, yielded only 0.38 per cent of crude wax. In 1918 Knecht and Hall[131], using an improved method of extracting cotton yarn with benzene in a large copper Soxhlet apparatus, obtained 0.407 per cent of crude wax from American and 0.444 per cent from Egyptian cotton. Tests of tensile strength showed removal of the wax increased strength and diminished the elasticity of the yarn.

In 1932 Knecht and Streat[132] found that only a portion of the cotton wax is on the exterior of the fiber, and that the remaining portion of it is only completely removed by disintegration of the fiber. They extracted raw cotton by three benzene extractions, with alternate hydrochloric acid (d 1.01 and 1.025) immersions, which gave for American cotton 1.22 per cent, Egyptian 0.92 per cent, Indian 0.89 per cent, Queensland 1.04 per cent, and Nigerian 0.96 per cent of extract. Raw cotton disintegrated by boiling 15 minutes in HCl (d 1.025), drying, and powdering, when extracted with benzene gave for American cotton 0.74 per cent, Egyptian 0.64 per cent, Indian 0.67 per cent, Queensland 0.60 per cent, and Nigerian 0.72 per cent of extract. When the cotton was mechanically disintegrated by grinding, American cotton gave 1.20 per cent and Egyptian 1.00 per cent extract. Cotton extracted with alcohol gave for American cotton 0.65 per cent, Egyptian 0.975 per cent, Indian 1.31 per cent, Queensland 1.83 per cent, and Nigerian 1.1 per cent extract. Subsequent benzene extraction gave 0.18, 0.155, 0.2, 0.29, and 0.35 per cent additional extracts respectively. They were able to obtain white waxes from the crude cotton waxes.

In 1943 Conrad and Neely[58] reported that they had obtained 0.48 to 0.63 per cent of wax on the dry weight basis for most cotton lints, and much higher yields (12.64 to 15.04 per cent) for Arkansas green cotton lint, var. *G. hirsutum* L., the shrub which yields upland or short-staple cotton. Green lint and high wax content were closely associated. These investigators favor the removal of wax from either green lint cotton or white cotton by extraction with 95 per cent ethanol, and then transferring the wax to chloroform from ethanol extractive which can be diluted with water to withdraw and retain the sugar constituents. In four hours of alcoholic extraction 0.61 per cent of wax was obtained from Egyptian cotton, and 0.72 per cent in 32 hours. The chloroform extract had taken up sugars only to the extent of 3 per cent of the total wax content of the cotton. Green lint cotton yielded 13 per cent of a lipid wax by the Conrad ethanol-chloroform method.

According to the Indian Central Cotton Committee Technical Laboratory,[1] the degree of silkiness of cotton may be expressed in terms of the wax content of the clean lint. Contents of different varieties of cotton—such as very silky above 0.500 per cent, silky 0.425–0.500 per cent, slightly silky 0.350–0.425 per cent, roughish 0.300–0.350 per cent, and rough below 0.30 per cent. The wax content of Kampala is 0.544, Punjab-American (*G. hirsutum*) 0.468, Navsari (*G. herbaceum*) 0.457, Palej (*G. herbaceum*) 0.405, Dholleras (*G. herbaceum*) 0.387, Kumpta (*G. herbaceum*) 0.359, Banosa (*G. neglectum*) 0.330, and Sind cottons 0.229 to 0.274 per cent.

In 1946 Tonn and Schoch[275], at the University of Texas, Austin, investigated a crude cotton wax obtained as a by-product of a pilot plant operation in which 100-pound batches of Texas cotton fiber were extracted with

hot benzene to obtain 25 pounds of wax from 10 bales of cotton. The wax has a dark greenish-brown color, which changes to a tone of yellow when decolorized with active carbon, fuller's earth, or a combination of the two. Without further refinement this semirefined wax has a characteristic disagreeable odor, and the consistency of beeswax. These investigators report the following analytical constants: melting point 68–71°C; specific gravity (d_{15}^{15}) 0.959; saponification number 70.6; acid value 32.0; ester value 38.6; acetyl value 73.1; iodine number 24.5; fatty acids 25 per cent; unsaponifiable 25 per cent; Hehner number 100; and Reichert-Meissl number 0 of the fatty acids.

Cotton linters wax obtained from the Southeastern U. S. cotton has an acid value 55, saponification number 125, iodine number 70, and hydroxyl percentage 1.0, from which by selective extraction of methanol and acetone, following the original extraction of the linters by heptane or like solvent, can be obtained a hard fraction of a deep yellow-brown color, having the following analytical constants: melting point (Drop Softening) 86.8°C; melting point (Fisher-Johns) 72.9°C; density (d^{25}) 0.998; density (d^{95}) 0.886; density coefficient 0.00188; acid value 31, saponification number 109; iodine number 11.0; percentage hydroxyl 1.0; penetration at 21°C, 200 g/10 sec 50.2; dielectric constant at 60 cycles 0.168, and at 1000 cycles 0.032; volume resistivity 6.8×10^{12} ohms cm.

Lamesa and Buckeye cotton lint when extracted with heptane yield a crude wax which upon methanol extraction, and two acetone treatments (7:1) yields 9 to 10 per cent of a hard fraction of 78°C melting point, acid value 23, saponification number 178, iodine number 17, per cent hydroxyl 2.2, and 30 to 40 per cent of a softer wax (m. 60°C). The crude has also been chemically treated to eliminate the unsaturated constituents; the resultant wax is of an olive-yellow color and has about the consistency of beeswax. It has an acid value 128, saponification number 153, iodine number *nil*, per cent hydroxyl 1.8, and melting point 62°C.

Kettering and associates, at the Southern Research Laboratory, New Orleans, Louisiana, where solvent extractions of many samples of cotton are made, state that the Conrad alcohol-chloroform extraction gives the more accurate determination of the amount of wax than the simple extraction methods.

Chemical Composition of Cotton Wax. The chemical composition of cotton wax has been extensively investigated, starting out with the early studies made by Schunck who in 1868 isolated a fatty acid melting at 55.5°C, and which he believed to be margaric acid, but which is now regarded as a mixture of *palmitic* and *stearic acids*. In 1911 Knecht and Allan[130] isolated from their so-called "glassy wax" (m. 78°C) two hydrocarbons of crystalline form; one melted at 68.1°C and was identified as

n-hentriacontane, and the other melted at 70°C and agreed in analysis with *n-dotriacontane*. From the acetylated alcohol of the unsaponifiable they separated a crop of crystals (m. 127.2°C) which they believed to be phytosterol. The presence of any substantial amount of phytosterol in cotton wax has not been confirmed.

The saponified portion of the wax yielded 0.21 per cent glycerol, a small quantity of an acid (C_{32}–C_{34}) which melted at 74.4°C, and both *stearic* and *palmitic acids*. The unsaponifiable of their "benzene-extracted dark green wax" yielded one-third of a reddish-brown sticky wax (m. 63.4°C), phytosterol (m.pt. of acetate 122.4°C), and a wax acid (m. 70.8°C, m.wt. 455) which they believed to be *melissic acid*, $C_{30}H_{60}O_2$.

In 1923 Fargher and Probert[77] treated American cotton in sliver form with redistilled 90 per cent benzene, heating it with superheated steam. Then by carefully treating the extract with selective solvents they obtained the alcohol, acid, and hydrocarbon components. In this manner they discovered a new alcohol, $C_{30}H_{62}O$, for which they proposed the name of *gossypyl alcohol*. *Montanyl alcohol*, $C_{28}H_{58}O$, was present in small amount, also *ceryl alcohol*, $C_{26}H_{54}O$, and *carnaubyl alcohol*. They also isolated *triacontane* as one of the hydrocarbon components. These investigators discovered that gossypyl alcohol occurs in three forms—α, β, and γ—of the following respective melting points: 87–88°, 86°, and 82–83°C, and solubilities 0.19, 0.43, and 1.09 grams in 100 ml ether at 25°C. These forms of gossypyl alcohol give identical derivatives when fused with potash lime, yielding the same acid. Gossypyl alcohol as a whole crystallizes from benzene in coffin-shaped needles, and from pure anilin in long thin blades. With a pyridine-anilin reagent it is precipitated as dianilin. The montanyl alcohol present on fusion gives montanic acid, identical to that found in montan wax. γ-Gossypyl alcohol has also been found in the corms of the Indian jackinthepulpit, *Arisaema triphyllum* (L.) Schott.

The acids in the free state include C_{16}, C_{18}, C_{26}, C_{28}, C_{30}, C_{32}, and C_{34}. The C_{30} acid is known as *gossypic acid*, and the C_{34} acid as *geddic acid*. The esters occur as ethers of saturated C_{24}, C_{16}, and C_{18} acids. The C_{24} acid occurs as *carnaubic acid*, the C_{16} acid as *palmitic* acid, and the C_{18} acid as *stearic acid*. Esters also exist of *oleic acid*, and a lower isomeride of oleic acid, but these unsaturated acids occur in very small amounts. The C_{34} acid present in cotton wax may be identical with that isolated by Schalfeef from beeswax, since it has the same melting point. Schalfeef was inclined to believe that the so-called melissic acid in beeswax is a mixture from which a C_{34} acid in the form of needles can be isolated. The alcohol corresponding to the C_{34} acid is incarnatyl alcohol (m. 72–74°C), isolated by Sundwik[256] from bumblebee wax, and by Rogerson[232] of London, from the flowers of *Trifolium incarnatum* L., the carnation or crimson clover.

Fargher and Probert[77] found that the phytosterols of the reddish-brown

sticky wax of Knecht and Allan consist chiefly of *sitosterol* ($C_{27}H_{46}O$), and small quantities of α- and β-amyrin ($C_{30}H_{50}O$). Sitosterol occurs as the corresponding glucoside, *sitosterolin*. Fargher and Higginbotham isolated from the wax of Egyptian cotton a different sterol from that found in American cotton and identified this new sterol as having the formula weight $C_{29}H_{50}O$, or higher than that of the ordinary sitosterol ($C_{27}H_{46}O$) It is also a component of the glucoside of the cotton.

The amyrins found in cotton and some other plant waxes are derivatives of terpenes; they do not combine readily with the higher acids, but do with ionizable acids, such as acetic, to form in this instance acetates. However, they are found as palmitates and less often as myristates and stearates in plant life (see Amyrins, p. 31).

The approximate composition of semirefined cotton wax is given in Table 47; it is based upon the results obtained by Tonn and Schoch and others.

Hemp Wax

Hemp is the bast fiber from the inner bark of the hemp plant, *Cannabis sativa* L. Misnomers are "Manila hemp" for abacá (*Musa textilis* Nées); "sisal hemp" for sisal or henequen (*Agave fourcroydes* Lem.); "New Zealand hemp" for phormium (*P. tenax* Forst); "Indian hemp" for roundpod jute (*Corchorus capsularis* L.), "Mauritius hemp" for furcrea fiber (*Furcraea gigantea* D. Diet.) (Vent.); and "Sunn hemp" for Sunn crotalaria fiber (*C. juncea* L.) none of which is true hemp.

Hemp wax, strictly speaking, is the wax of the common hemp, *C. sativa*,

TABLE 47. APPROXIMATE COMPOSITION OF SEMIREFINED COTTON WAX

Alphyl Esters of Wax Acids:	46–47 per cent
Esters of mixed acids (mean m. wt. 662), C_{24}–C_{34} alcohols, and C_{16}–C_{34} acids	
Free Acids:	25–26 per cent
Aliphatic monocarboxylic, C_{16}–C_{34}	
Triterpenic resin acids (large amt.)	
Sterols and Resinols (free and combined):	10–12 per cent
sitosterol, $C_{29}H_{50}O$	
α- and β-amyrin, $C_{30}H_{50}O$	
Glycerides:	1–3 per cent
Olein (principally)	
Hydrocarbons:	7–9 per cent
Triacontane (small amt.)	
Hentriacontane	
Dotriacontane	
Carbohydrates, Moisture, etc.	2–3 per cent

Note: When cotton wax is highly refined the alphyl esters content is greatly increased, and the glycerides and carbohydrates practically eliminated; the sterols, resinols, and resin acids are greatly reduced.

an annual dioecious plant, and the only species of *Cannabis*, family *Moraceae*. Hemp is cultivated as an annual crop almost everywhere in the world. The bast fiber of commerce is produced by retting and scutching of the hemp stalks. All of the other hemps mentioned also contain wax. The wax is produced from the dustings obtained in scutching.

The hemp stalks, either dew-retted or water-retted, after drying, are fed to power-driven machines, in which handfuls of retted stalks pass endwise between rapidly revolving fluted rollers. The fiber is then held by hand so that the loosened hurds (small pieces of the woody portion) are beaten away by smooth projections on revolving cylinders; a considerable amount of dust results from the mechanical operation. This dust contains a fairly large quantity of fat-wax mixture which is extractable by benzene or other suitable solvent. The wax when purified has a melting point of about 69°C, acid value 22.2, saponification number 86.3, iodine number 33.3, and unsaponifiable 13 per cent[169]. The low percentage of unsaponifiable is due in part to a relatively high percentage of glycerides and resinols.

A wax of hemp waste of the plant (*C. sativa*?) cultivated in Poland from Yugoslav seed has been produced with a melting point of 73–74°C. The bast fiber of hemp produced in Korea by steaming and scutching by hand, has a length of 1.2 to 1.3 meters and is 0.6 to 0.7 mm in breadth. It is light yellow in color. Its fiber consists of pectocellulose, lignocellulose, water extractables, and 1.25 per cent of fat-wax mixture. Ambari (Deccan) hemp, *Hibiscus cannabinus* L., of India and East Indies belongs to the family *Malvaceae*, and yields a wax concerning which not much is known.

Bianchi and Malatesta[28] described a waxlike fatty substance produced from hemp fibers. It is brown in color and of a conchoidal fracture. The wax has the following characteristics: specific gravity (d^{15}) 1.0190; melting point 66–67°C; acid value 46–47; ester value 145; iodine number 22.2–22.8; saponification number 162.6 (rising to 187–192 on prolonged treatment); and unsaponifiable (m. 60°C, d^{15} 1.0022) 11 per cent.

Since hemp wax has a very low amount of unsaponifiable substance it contains only a small amount of *monohydric alcohol-acid esters*, and little or no hydrocarbons. It contains resin acids, *free fatty acids*, and a large percentage of *glycerides*. It contains *sterols* and/or *resinols*. An approximate composition of hemp wax would be: combined alcohols (straight chain and cyclic) 12–15 per cent (calc. as amyrin derivative); 8–10 per cent resin acids; 11–14 per cent free fatty acids (calc. as palmitic); and 65–70 per cent glycerides (calc. as palmitin).

Sisal Wax

The wax of henequen, or sisal (sisal agave), *Agave fourcroydes*, an African variety of *A. rigida*, and quite similar to the Yucatan variety *sisalana*, is

becoming of economic importance. Sisal or henequen is one of the chief crops grown in East Africa. During World War II a peak production of sisal of 130,000 tons per annum was achieved. The fiber and tow are products of established commercial value. The waste discarded during decortication can be used for producing wax pectins and pectates, fermentable sugars, and other products. The wax has been recovered by the African Sisal and Produce Company, Ltd. There are large sisal estates in Kenya and Tanganyika which will have their own waste-treatment plants.

In its production the wax is removed with the softer parts from the fibers of the leaves by a machine equipped with scraping wheels. The value of the wax according to Walsh *et al.*[308] can be enhanced by increasing its melting point through treatment of the wax in its molten state with an acidic reagent, such as sulfur dioxide or a metallic chloride (Fe, Zn, or Al). If the wax is in a molten condition it is treated with the acidic agent at 165°C or thereabouts; if in solution the solvent must be inert and of sufficiently high boiling point to withstand a temperature of not less than 85°C for the heat treatment.

Sisal wax may also be extracted from the surface of uncrushed sisal leaf by a solvent, the leaf preserving its original fiber structure. The solvent used is preferably anhydrous and immiscible with water, e.g., chloroform, diethylene chloride, carbon tetrachloride, etc. The solvent in vapor form is brought into contact with the leaf and then condensed to liquid form; the extraction is carried out at 50°C. Sisal fiber is separated after the surface solvent extraction by decorticating the hot, limp leaf without crushing the pulp. The refined wax has a crystalline structure. [Brums, P. F., British Patent 675,001 (1952).]

Sisal wax has properties similar to those of the sisal hemp wax of Yucatan.

The African Sisal and Produce Co., Ltd. possesses certain patents relating to the treatment of the flesh of the sisal, after removal of the main bulk of fiber, for the recovery of wax. The treatment consists of first air-drying and then heat-drying (105°C) the flesh; extracting the dry flesh with an organic solvent (e.g., $CHCl:CCl_2$) at a temperature below the boiling point of the solvent; and refluxing the condensed solvent vapor according to the treatment used. The wax is obtained by distilling off the solvent [*C.A.*, **41**, 6741 (1947)], and then treated with an acid reagent for purification, as taught by Walsh and associates[308].

Wax of Sisal Hemp of Yucatan

The sisal hemp, *Agave sisalana*, family Amaryllidaceae, of Yucatan, contains an appreciable amount of wax. This shrub is cultivated in tropical countries for its fiber which can be used as a substitute for hemp. According to Legg and Wheeler[152] cuticle of the leaf contains 20 per cent of wax. Politzer[209] reports that when toluene is used as a solvent to extract the hard

wax of the cuticle of the leaf it is obtainable with a 17.43 per cent yield, as contrasted to 1.73 per cent obtained from the stripped leaf.

Best yields were obtained by Politzer from the carding flume tow prepared by retting. Two to three pounds of wax could be recovered from 15 pounds of the waste accumulating from each short ton of fresh leaf. Benzene is selected in preference to many types of solvents, inclusive of toluene, as the one best suited for large-scale extraction.

The wax of sisal waste has the following characteristics: specific gravity (d^{15}) 1.007–1.010; setting point 80–81°C; acid value 16–19; saponification number 56–58; iodine number (Hanus) 28–29. Politzer[209] found that the portion of a benzene-extracted wax which is soluble in the cold had a higher melting point (81°C) and acid value (19.4) than the insoluble portion (m. 62–63°C, acid value 2.1). The chemical composition appears to be a mixture of a considerable amount of *montanyl* and *myricyl alcohols*[152] which may be combined to some extent with *palmitic acid* as esters. The high iodine value indicates a considerable amount of unsaturated compounds, particularly in the softer wax component, which is soluble in cold alcohol. The alcohol-insoluble component has a setting point of 80°C. The presence of *hydrocarbons* is indicated.

Broom Wax

The tops of Holland broom, or Scotch broom, *Cytisus scoparius* L.; the Algerian broom, or weavers-broom, *C. junceus* (*Spartium junceum* L.); and other brooms of the family order *Papilionaceae*, contain fatty, resinous and waxy substances. This extractable waxy material amounts to about 2.5 per cent of the weight of the tops. In the production of paper pulp from the broom, Lüdecke[109] proposed extraction of the offal to recover the lipid wax instead of losing it in the waste water at the pulp mill. This investigator found that the extractable, by solvent means, from the offal of Holland broom amounted to 25.6 per cent of a wax with 64°C melting point.

The fibers of broom after retting and scutching are used to produce cordage and strong fabrics. The lye used to boil broom to separate the fibers, when treated with sulfuric acid, yields a precipitate from which a fat-and-wax mixture can be extracted with a solvent. The wax yield is greater with an increase in concentration of the lye and the boiling time.

Cauassu Leaf Wax

The cauassu (caauassu), or cauaçú, *Calathea lutea*, a perennial shrub of the family Marantaceae, has many large broad leaves, the lower surface of which are coated with a hard wax. The cauassu, which resembles a banana plant, grows in certain regions of the Amazon Basin, particularly in the area of Garupa, Brazil. The Indian name for "big leaf" is "cauassu";

hence the common name. The shrub according to Knaggs[128] is easily cultivated and at maturity produces about 100 kg of wax per ha. Steinle[259a] states that 7000 seedlings can be planted within an area of about 10,000 square feet and harvesting may begin just a year after planting. In subsequent years two harvests may be collected annually, thus producing about 200 pounds of crude wax each year.

After the leaves are dried for three days, mechanical beating removes the bulk of the wax. The wax that remains is removed by immersing the leaves in hot water for 30 minutes, then skimming off the wax.

The wax separated from the leaves has a melting point of 80.5–86.0°C. It is somewhat resinous, has an acid value 11.2–12.3, saponification number 39.6–29.0, ester value 28.4–16.7, and iodine number (Hanus) about 16. Pegorari[205] states that the wax is partially soluble in chloroform, leaving a residue of about 10 per cent of insoluble. The wax loses 1.5 to 1.9 per cent of its weight in drying, and has a hardness which is said to be comparable with carnauba wax.

Wax of Spanish Moss

Spanish moss, *Tillandsia usneoides* L., which is also called Florida moss, contains a wax. The hard, resilient inner fibers are used extensively in the upholstery industry, the remainder of the plant being discarded or utilized as compost. Schroger[245a] in 1927 reported the presence of a green-colored wax in Spanish moss. Feurt and Fox[78a] state that the freshly gathered moss contains about 5 per cent of wax. The wax has a saponification number 120.4, acid value 25.0, ester value 95.0, and iodine number 33.0. It is soluble in various organic solvents, extractable from waste material, easily purified, and imparts a hard, glossy finish to woodwork and leather, say these investigators. The wax is hard and melts at 79–80°C.

Wax of Indian Sorrel

The petals of the cultivated Indian sorrel of the Orient, or of the similar plant known as jamaica, or roselle, of Mexico and Texas, both *Hibiscus sabdariffa* L., contain wax. The plant yields "roselle fiber," and the calyx which is mucilagenous is used in jelly making. Murti and Seshadri[196c], of Andhra University, India, extracted the petals of *H. sabariffa* with boiling alcohol, and added the concentrate to a large excess of boiling water. From the sticky solid material they isolated an ether-soluble lipid wax. Little is known of its composition other than that its unsaponifiable contains hydrocarbons, namely C_{27} and homologs.

Wax of Indigo Plant

The indigo plant, *Indigofera linifolia* Retzius, of the family Papilionaceæ, yields a wax with a melting point of 78–79°C. When the plant is extracted

with alcohol, an unsaturated lactone ($C_{28}H_{50}O_2$, linifolin, m. 95–96°C); a wax; tannin; phylopaphene; and glucose, have been found in the extractive matter. This lipid wax has a constituent with the chemical composition $C_{42}H_{84}O_2$, indicating it to be a ceryl ester of palmitic acid, namely *ceryl palmitate*[94]. Since ceryl palmitate melts at 69°C, it is obvious that the wax must contain still higher melting point constituents.

Wax of Kohlrabi

Kohlrabi, *Brassica oleracea italica* L., contains two waxlike compounds, one melting at 64°C, and the other at 73°C. They are found only in very small amounts and then in the more mature plants.

Wax of Wild Senna

Leaves of the European wildsenna, or globedaisy, *Globularia alypum* L., contain a waxy lipid, which Jacini[118] has attempted to identify. The leaves were extracted with boiling ether and yielded 13.3 per cent of a gray-green viscous extract; the extract lipid wax was fractionated, so that its components could be isolated. The chief constituents proved to be a hydrocarbon, $C_{30}H_{62}$ (m. 65°C), which constituted about 20 per cent of the total extract, and *ceryl alcohol* ($b_{0.02}$ 175°C, m. 80.5°C) which constituted 15 per cent. Jacini also isolated *palmitic acid*, *linoleic acid*, *cerotic acid*, and a new type of *ricinoleic acid*, $C_{17}H_{31}CO_2H$.

Wax of Garden Sage

It is recorded that the leaves of the garden sage, *Salvia officinalis* L., contain 0.57 per cent of wax. The wax contains a white crystalline substance (m. 278°C) of triterpenic structure, believed to be identical to α-ursolic acid. The same substance is found in the leaves of the common periwinkle, *Vinca minor* L.

Tea Wax

A lipid wax can be extracted from the leaves of the common tea plant, *Camellia sinensis* (*Thea sinensis* L.), and the allied plants, sasanqua camellia, *Camellia sasanqua* Thunberg (*T. sasanqua* Nois), and Japanese rose camellia, *Camellia japonica* (*T. japonica* L.), the latter the source of tea seed oil of commerce. Tea leaves contain wax, resin and fixed oil, wax being in the smallest amount—less than 0.15 per cent.

A specimen of tea wax may be found on exhibition at the Field Museum, Chicago. It is black in color, and plastic in consistency. Small quantities of tea wax have been offered from abroad to the tea importers in New York. Tea wax is said to be emulsifiable, and of possible usefulness in the food industry.

The chemical composition of tea wax is not fully known. It has been

reported to contain a sterol named *theasterol* (m. 167–168°C, acetate m. 180–181°C) linked with daturic acid, $C_{17}H_{34}O_2$. The presence of the latter acid in a natural wax is open to question, since a C_{17} composition is likely to be a mixture of C_{14} to C_{20} acids, each of an even number of carbons; possibly *palmitic* and *arachidic acids* predominate—or a C_{17} composition might well be a methylated fatty acid, namely *isomargaric acid* (m. 55°C). The wax unsaponifiables according to Ikeda[112a] also contain so-called "thea-alcohols." These have the formula $C_nH_{2n+2}O$, where n ranges from 28 to 32. The alcohols, A, B, and C have melting points of 82–83°, 84–85°, and 92–92.5°C respectively. Other constituents are hydrocarbons C_{29}–C_{31} (m. 65–65.5°C) and β amyrin, $C_{30}H_{50}O$ (m. 198–199°C), and some unsaturated oil substances. The wax has also been reported to contain the monoethylene alcohol *nonenol*, $C_{19}H_{17}OH$, and traces of carotenoids and squalene[259].

Wax of Coca Leaves

The leaves of the cocaine tree, *Erythroxylon coca* Lamark, *E. novogranatense* Morris, and *E. truxillensis* Rusby, family Erythroxylaceæ, are reported to contain a wax. The coca leaves of these species are commonly known as Huanuco, Peruvian, and Trujillo. The wax is possibly of only academic interest. The Huanaco variety of coca is grown in Bolivia Huanaco (Peru), Brazil, Venezuela, and Argentina; the Trujillo coca variety comes chiefly from northern Peru. Historically, the discovery of the wax is credited to one Albert Niemann of Goslar, Germany who made the first thorough investigation of the leaves, and gave to the alkaloid the name it now bears—cocaine. Niemann reported that coca leaves contain a wax, a tannic acid, and a concrete volatile odorous substance. The wax can be extracted from the dried leaves by means of hot alcohol in which the wax is reputed to be very soluble. The wax melts at 70°C, and is reported to have the ultimate composition, $C_{33}H_{66}O_2$. A terpene, *erythrodiol*, $C_{30}H_{50}O_2$, has been isolated by Zimmermann from Peruvian leaves; it occurs as a monostearate, namely *erythrodiol stearate*.

Wax of Orange Leaves

The leaves of the sweet orange, *Citrus aurantium* L., when extracted with benzene yield 1.1 per cent of a waxy concrete from which on steam distillation 10.9 per cent of a volatile oil of delicate odor is obtained. The dark green wax after distillation has a melting point of 63°C, and contains 25.2 per cent hydrocarbons (m. 75–76°C).

Wax of Yerba Maté

The leaves of yerba maté, or paraguay tea, botanically classified as *Ilex maté paraguariensis* St. Hilaire, and which is a member of the holly family, contain a wax. The leaves of the maté shrub, which is indigenous to Brazil

and Argentina, when dried are used like Chinese tea, but prepared in gourds with bombillas. Caffeine is commercially produced from maté by mixing the leaves with lime and extracting the mixture with benzene from which extract the caffeine is removed with water. Raoul[226] states that evaporation of the benzene yields a greenish crude wax.

In 1944 Paula[204] extracted maté infusions with petrolic ether, benzene, and other solvents, and obtained from 8.3 to 13 per cent extractives, the unsaponifiable portion of which represented 4.6 per cent of the maté. Fifty per cent of the unsaponifiable portion was α-amyrin (f.p. 176–180°C, $[\alpha]_D^{23}$ + 92°). By chromatographic adsorption with alumina and activated magnesia Paula isolated 2.5–3 per cent of a soft white wax [f.p. 36°C; index refraction (n^{15}) 1.5155; acid value 0.35; saponification number 78.54]. The wax of Raoul has a much higher melting point that that of Paula indicating the presence of a considerable amount of the α-amyrin. Raoul noted that the unsaponified portion (61.08 per cent) of the greenish crude wax consists almost entirely of *phytosterols* and on acetylation yields crystals with a melting point of 135.2°C.

Raoul[226] gives the following constants for the crude wax of maté: melting point 59–65°C, specific gravity (d^{15}) 1.008, index of refraction (n^{15}) 1.4698, saponification number 110.14, acid value 11.79, acetyl number 68.60, fatty acids 58.54 per cent, unsaponified 41.78 per cent. When the crude wax is extracted with petrolic ether the soluble portion (81.32%) consisted of soft solids (m. 18–30°C, d^{15} 0.990, acetyl number 169, unsaponified 61.08 %). Raoul states that the crude wax when treated with chlorine produces a rubber-like product.

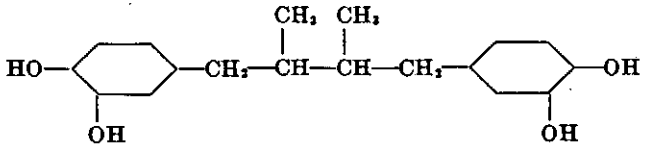
Uva Ursi Wax

A wax is extractable from the leaves of the *Uva ursi* L., a well-known drug. The low evergreen shrub is commonly called "bearberry." If the leaves are extracted with ether, *ursolic acid* may be isolated. This acid is probably identical with that obtained from the skin of the cranberry, and has a melting point of 284–285°C. However, the derivatives on methylation melt at 230 and 172°C respectively, and the acid is thought to exist in β and α modifications, or isomers which have melting points of 290–291° and 283°C respectively. *Oleanolic acid* (m. 290–291°C) which belongs to the β amyrin group is generally regarded as the equivalent of β-ursolic acid.

Wax of *Larrea* Leaves

The surface of the leaves and stems of the spreading creosotebush, *Larrea divaricata* Cavanilles, contains a lipid wax. The plant is indigenous to the southwest desert areas of the United States and Mexico. It is commercially extracted for its content of *nordihydroguaiaretic acid* (N.D.G.A.), an ex-

cellent antioxidant for lipid food products. The acid is also chemically known as 4,4′-(2,3-dimethyltetramethylene) dipyrocatechol ($C_{18}H_{22}O_4$, m. 184–185°C), and has the structural formula



According to Waller and Gisvold[206a], the wax is composed chiefly of esters of a mixture of C_{26} and C_{28} acids and mainly C_{30} alcohol. The unsaponifiable portion of the petrolic ether extract yielded a small amount of sterol fraction (m. 126–128°C) which apparently is a mixture. A yellow flavonol (m. 217–218°C) and an orange-colored flavonol (m. 230–232°C with decompn.) were isolated. The wax also contains an appreciable amount of amorphous phenolic substance which comprises about 50 per cent of the resinous material (ostensibly nordihydroguaiaretic acid).

Wax of Hoarhound Leaves

The surface of the leaves and tops of hoarhound, *Marrubium vulgare* L., contains a wax. The dry leaves are extracted with acetone, and upon evaporation of the solvent, and residue is extracted with ethyl ether from which on cooling "marrubine" is obtained. The mother liquor contains chlorophyll and waxy material. Upon evaporation a residue is obtained which is partially soluble in ethanol. The insoluble portion gives a wax on refluxing.

Wax of Arbutus Leaves

The surface of the leaves and stems of the strawberry madrone (tree), *Arbutus unedo* L., family Ricaceae, is covered with a waxy material. Extraction of the foliage with hot alcohol by Sosa[257b] yielded 1.76 per cent of a greenish-white waxy product. The crude wax when extracted in a Soxhlet apparatus with ether gave a colorless waxy substance, which when recrystallized from ethanol followed by ethyl acetate yielded about 0.2 per cent (based upon foliage) of a white wax solid (m. 74°C). The crude wax contains hydrocarbons, higher aliphatic alcohols, triterpenic acids, sterols, chlorophyll, yellow lipoid pigments, etc.

Sosa[257a] was able to isolate several constituents from the white wax (m. 74°C) by means of chromatographic analysis. The wax when dissolved in benzene and chromatographed on alumina gave three fractions. From the first fraction (m. 67°C) constituting 57 per cent he recovered *hentriacontane* (m. 69°C) by recrystallization. From the other two fractions (14.5%) aliphatic alcohols, namely *myricyl* alcohol ($C_{30}H_{61}OH$, m. 86°C, acetate m.

74–75°C), and *lacceryl alcohol* ($C_{32}H_{63}OH$, m. 89°C, acetate 76–77°C) were isolated.

On standing, the alcoholic mother liquor from the second fraction deposits needles (m. 280°C) which then purified by recrystallization were identified as those of *ursolic acid*. Sosa reported that ursolic acid may be obtained directly from the crude wax by chromatographic procedures should the occasion arise.

A solution of 3.7 g of wax (m. 79°C) isolated from the alcoholic extract of 2 kg of stems, when chromatographed, yielded 1.52 g of $C_{31}H_{64}$ (hentriacontane), a yield of about 41 per cent. There was also recovered by selective solvents washings a C_{29} alcohol ($C_{29}H_{59}OH$, m. 84°C, acetate m. 69°C), which apparently corresponds to *d-nonacosanol* (m. 83.8°C).

Sosa[257b] had previously reported isolating a new sterol, or resinol, from the waxy substances of arbutus leaves to which he gave the name of *unedosterol* ($C_{29}H_{47}OH$, m. 218°C, $[\alpha]_D^{20}$ 29.1° in $CHCl_3$) ostensibly a triterpenoid. He also had isolated an acid of cyclic structure ($C_{36}H_{68}O(OH)COOH$, m. 256°C, Ac. deriv. m. 176°C), which he termed *arbutolic acid*.

Wax of Baccharis

Baccharis is a genus of aromatic plants, which are shrubs with small flower heads, belonging to the family order Compositae. There are many well-known species. Kurz, Jr.[146] isolated a lipid wax from the broom baccharis, *Baccharis sarothrides*. The wax has a relatively high melting point, 83.5°C, and high iodine number, 53.9, indicating the presence of *resinols* in its composition.

Wax of Goldenweed

Wax has been reported as a constituent in two species of goldenweed namely the larchleaf goldenweed, *Aplopappus laricifolius*, and *A. tenuisectus*, by Kurtz, Jr.[146] The wax melts at 66.5°C. To obtain the wax the dried plant was extracted with petrolic ether, and the extract was treated with acetone to separate it into lipid wax and nonwax fractions.

Waxes of Succulent Plants

Madagascar Waxes

Waxes are produced in Madagascar from plants botanically classified by Herbert and Heim[102] as *Cynanchum messeri*, *Euphorbia xylophylloides*, and *E. stenoclada*. The dried-out pieces of plant stems are pounded on a cloth and then thrown into boiling water; the wax is skimmed off as it floats to the surface. *C. messeri* Asclep., a species of swallowwort, yields the most wax—about 7 oz from six small plants. One of the waxes, *E. stenoclada* Baill., is obtained from a tree commonly known as the "rhimba tree."

TABLE 48. PHYSICAL CHARACTERISTICS OF MADAGASCAR WAXES

	Swallowwort (*C. messeri*)	Flatstem Euphorbia (*E. xylophylloides*)	Rhimba tree (*E. stenoclada*)
Melting point (°C)	88.0	88.0	88.0
Acid value	17.7	28.0	19.3
Sapon. number	159.6	142.8	140.0
Iodine number	3.2	5.3	5.9
Hydrocarbons (%)	11.0	14.0	15.0

Madagascar *rhimba wax* appeared in commerce some years ago in the shape of small irregular masses adhering to pieces of bark from the tree. Botanically, the plants are related to those which produce candelilla wax, but in chemical composition the constituents are in vastly different proportion. The Madagascar waxes have a lower hydrocarbons content, and are low in iodine number, indicating the absence of an appreciable amount of unsaturated compounds. The melting points of the Madagascar waxes are higher than those of any other natural waxes.

The latex of the gum euphorbia, *E. resinifera* Berg, in Morocco contains 33–36 per cent of solids. The solids contain 28–30 per cent of wax; the balance comprises rubber hydrocarbons, resins, water-soluble substances, and mineral matter. The wax melts at 67°C.

The chemical composition of the Madagascar waxes is not fully known. It has been reported that they contain an appreciable amount of alcohols in the C_{26} to C_{32} range in a free state. These waxes are believed to contain esters of *sitosterol* with hydroxylated acids, but the amount is small. The Madagascar waxes contain free or combined acids which in part are resinous; they also contain hydrocarbons of C_{31} and higher carbon content.

(3) WAXES OF GRASSES AND SEDGES

Waxes of grasses, *Gramineæ*, include those derived from canes, e.g., *Saccharum officinarum* L.; forage grasses, e.g., *Medicago sativa* L.; fiber-yielding grasses, e.g., *Stipa tenacissima* L.; and cereal blades, e.g., *Sorghum vulgare* Persoon.

Although the wax content of the grasses is a mere fraction of one per cent, some of the grasses are handled in such immense tonnages for utilization of whatever constituents there may be a preponderance of (e.g., sugar, starch, protein, or cellulose), that it sometimes proves economically sound to recover the wax from the by-product waste material obtained in the recovery processes.

In this category is sugarcane wax of *S. officinarum*; esparto wax of *S. tenacissima*; and sorghum-grain wax of *S. vulgare*. Forage grasses are consumed as such, and do not contain sufficient wax to make its recovery economical; and the sedges rarely contain wax.

Waxes of Canes

Sugarcane Wax

Sugarcane wax is the whitish to dark-yellowish powdery deposit on the surface of the stalks of the sugar cane, *Saccharum officinarum* L. An apothecary by the name of Avequin[14] of New Orleans, Louisiana, was the first to isolate and purify the cuticle wax (1841). He gave it the name of "cerosin," or *cerosie*.

During the milling of the cane, a large portion of the powdery substance becomes detached, and mixed with the expressed juice as an insoluble suspended impurity, and finds its way into the "cachaza" or filter-press mud, from which it can be economically recovered. The remainder of the wax, nearly 60 per cent, is left in the "bagasse," which is the waster obtained after expressing the juice. The actual amount of wax in sugarcane is not much over one-tenth of one per cent by weight, and most of this wax is near the nodes of the cane.

Investigators in the past have proposed to recover sugarcane wax from four different sources, although the fourth source mentioned below is the only one exploited on an extensive scale in the United States. The following methods for the recovery of wax from the various sources include (a) extraction directly from the cane, (b) extraction from the raw juice, (c) extraction from the begasse, (d) extraction from the cachaza, or defecation mud.

(a) *Extraction from Cane.* A wet method of extracting the wax from the uncrushed stalks was proposed by Bunker[44]. In this method the stalks are propelled through a tank of hot water which flows in the opposite direction; while submerged the wax separates and collects as a film on the surface of the water. This collected material is then floated into a recovery apparatus which Bunker has described in detail. A dry method was proposed by Wynberg[324] in 1911. This method involves a mechanical procedure of shaking the cane and blowing out the loosened wax.

(b) *Extraction from Raw Juice.* Cross, who has made numerous studies concerning the recovery of wax from sugarcane, proposed that the raw juice before deliming or sulfitation be treated in centrifugal-subsiders, and thereby the suspended solid matters, including wax, would be deposited in the drum, instead of passing into filter presses. The wax can then be extracted from the centrifugal deposit by boiling with denatured alcohol, filtering and chilling out the wax. By the Cross method most of the wax of the sugarcane could be effectively recovered.

(c) *Extraction from Bagasse.* The bagasse which leaves the last mill in milling cane contains about 45 per cent of water, 50 per cent of fiber, 2 to 4 per cent of unextracted sucrose, and a small amount of wax. Since bagasse is handled for conversion into cellulosic material for many uses in-

clusive of paper making, Simmons proposed that the wax be extracted at the time such conversion takes place. In the Simmons procedure the bagasse is digested with sodium hydroxide under 12 to 30 lb steam pressure, then washed, redigested with the caustic at 40 lb pressure and again washed. The residual washed fiber is converted into paper pulp, and the cane wax is extracted from the caustic solution by concentrating this to one-fourth of its volume and allowing the wax to rise to the surface of the scum. The scum is then removed by skimming ladles and purified in any convenient way. The yield is not over 0.5 per cent.

(d) *Extraction from Filter-Press Cake.* It is ordinary practice to lime the juice which is expressed from the sugarcane. On liming the juice the precipitated nonsugars carry down the suspended particles of wax, which thus pass into the sediments in the settling tanks, and finally into the filter-press cakes, which are made up of fiber, wax, starch, etc. The expressed juice of the cane contains, aside from 12 to 16 per cent of dissolved sugars, a considerable amount of colloidal nonsugars, and holds in suspension fine shreds of bagasse, wax, clay, and other material. The wax is extracted from the filter-press cake by a hot petroleum solvent, such as a high-boiling naphtha; the wax deposits on cooling and can thus be removed from the chilled liquid. The yield is from 5 to 17 per cent of crude wax. The basic method of recovering and fractionating the wax cake by solvent extraction was patented in France by A. Wynberg [French patent 397,843 (1909)].

South African Cane Wax. One of the earliest sugarcane wax recovery operations was that at Durban, Natal, Union of South Africa, established in 1914–18. The yield of crude wax from the dry mud press cake was 14 to 17 per cent. It was reported that in 1924 the plant at the central there produced 6000 tons of a dark-colored wax per annum for export.

A report in 1937 from the American consul, John Corrigan, at Durban, made to the U.S. Department of Commerce stated that up to the time of the revolution in Russia, the latter country was the principal market for sugarcane wax produced in Natal, as it was utilized for the manufacture of candles used in the Orthodox churches. Following the success of the Bolshevist revolution and the war on religion, the demand for the wax dropped rapidly; and as no markets other than this particular one could be discovered, the plants about Durban were forces to shut down. Since that time, no cane wax had been manufactured in Natal. In making a substitution of beeswax in a candle formula, less of the cane wax would be used, since the latter is harder and brittle, somewhat like candelilla wax. It was estimated by C. G. Smith & Company, Ltd., of Durban that it would require an expenditure of £10,000 to re-establish the plant of the principal producers in order to again produce the wax in volume. The wax was quoted by Smith a £30 per ton of 2000 lb f.o.b. Durban.

Recovery of Wax from Dry Mud Press-Cake. The most economical

method of those described is the fourth, in which the wax is recovered from the press-cake. The juice as stated is chemically treated with lime-cream, or other chemical agents for its clarification; the mixture is brought to a boil and discharged into settling tanks, known as subsiders, or clarifiers, before the sediment known as "clarification mud" or *cachaza* is pumped through the filter presses, thereby yielding clear filtered juice and cakes of solid matter.

Since sugarcane wax is quite soluble in hot benzene (or toluene) and but sparingly soluble in the cold, it is possible to partially free it from the oily matter which is more freely soluble. The crude cane wax obtained through benzene extraction must be later purified to a paler resin-free useful wax. For the recovery of the crude cane wax the press cake from the filters is carefully dried to a moisture content of less than 9 per cent, pulverized, and heated with a suitable quantity of benzene. After settling and decantation the hot benzene extract is filtered and allowed to cool. The crude cane wax separates out and is recovered by a second filtration (see also heptane solvent extraction, p. 224).

The crude cane wax is very dark in color since it contains fatty oil (30%) and a black resinous pitch (20%). The solvent evaporated from the filtrate is recovered for reuse. The crude cane wax is then refined (see Sugarcane Wax Refining Methods, p. 221). The soluble fatty oil fraction is recovered as a green semifluid pasty material.

Wet extraction of cachaza has been proposed by Rhodes and Swenson[230]. The cachaza should have a water content of from 60 to 85 per cent, and should be extracted with about five times its weight (dry basis) of solvent, such as toluene, held near its boiling point. According to Harding[95], sugarcane stalks contain 0.1–0.25 per cent of crude wax and almost as much fat, namely 2–3 pounds per ton of cane.

Waste filter press cake that remains after the cane is crushed and the juice clarified contains 3–19 per cent of the wax, depending on the variety of cane and the method of processing. Nearly 9 tons of air-dry press cake remain after 1000 tons of sugarcane has been processed. From this, 1600 pounds of crude wax can be recovered which yields dark hard wax and pitch[96] (see Sugarcane Refining Methods).

Benzene is a better solvent for the wax from defecation muds than toluene, naphtha, or heptane.

Sugarcane Wax Refining Methods. The crude sugarcane wax separated from "clarification muds" as previously described requires further treatment to free it from oily matter and resins. The general commercial procedure is to disperse the crude wax in a solvent (such as isopropyl alcohol) which readily dissolves the fatty oil fraction and leaves the hard wax and resinous matter as the suspended solid. This slurry is filtered to remove

the soluble fatty oil fraction which is recovered as a green semifluid pasty material. The semicrude insoluble wax containing resinous matter is reslurried with additional solvent and heated until the cane wax melts. At this temperature the resinous matter separates from the wax and is removed by decantation. The light layer containing the sugarcane wax is then evaporated to remove all the solvent, leaving the refined sugarcane wax which may be cast in pans or run into wax slabbing equipment. It has a melting point of 76 to 72°C.

Several investigators have promulgated different solvents for use in purifying the crude cane wax. The use of *acetone* is referred to in the Balch method and that of Swenson[268]. The latter also refers to the use of *methyl ethyl ketone*. McLoud[187] found that when *methanol* is used to separate the wax fraction from the sparingly soluble resinous fraction, the mixture of 40 parts of methanol to 10 parts of the crude cane wax should be heated to about 95°C under sufficient pressure to keep the methanol in the liquid phase, and the heating continued until the wax fraction goes into solution. The immiscible phases formed are then separated into the wax and resinous fractions. The waxy fraction when stripped of its solvent melts at 75°C.

Broeg and Balch[38] have noted that when *acetone*, *methanol*, or *ethanol* are employed as selective solvents, they should be anhydrous. But if *isopropyl alcohol*, *butyl alcohol*, or *ethyl acetate* is used, the solvents should be of 95–99, 80–90, and 90–95 per cent strengths by volume respectively, water being used as the diluent in each case. The use of paraffin solvents for extracting wax from filter press cakes was proposed by Clatcher, and for purifying crude cane wax, by Swenson[268]. They cannot be advantageously used since the operations must then be conducted under pressure.

From a practical operating viewpoint the use of isopropyl alcohol is preferable to methanol, ethanol, or *n*-propyl alcohol. McLoud[187] treated 200 lb of crude cane wax with 1000 lb of *isopropyl alcohol*. The mixture was then heated to 80–82°C until the wax fraction went into solution. Two immiscible phases were separated by decantation. The light layer was then evaporated; the final traces of isopropyl alcohol were removed in a batch vacuum evaporator. The residue left after evaporation was a brittle, brown, waxy fraction having a melting point of 75°C. The recovery was about 70 per cent. The heavy layer after stripping the solvent was found to consist of a black pitch-like resinous material without a defined melting point. but which softened at 100–160°C. This fraction constitutes about 30 per cent.

Wilder[322] suggested treating the crude cane wax with about eight or more times of its weight of *propyl alcohol*, or preferably *isopropyl alcohol*, at a temperature sufficient to place the wax portion in solution while maintaining the propyl alcohol in the liquid phase, then separating the insoluble

portion, while the waxy portion remains in solution. The filtrate may then be cooled to 35°C to precipitate the hard wax, and the latter then separated from the soft fraction. For example, 20 parts of crude wax were placed in a vessel together with 157 parts of isopropyl alcohol, and heated to a temperature of 81–83°C until the dispersion was complete. While hot the wax-solvent mixture was filtered, and a resinous portion (18%) was removed. The filtrate was cooled to 27°C and refiltered. The de-resinated hard fraction (41.5%) was recovered as filter cake and washed by additional isopropyl alcohol before drying. The soft fraction (40.5%) was recovered from the filtrate by stripping it of solvent.

In the refinement of crude sugarcane wax by the Wilder procedure, 1600 lb of crude cane wax are said to yield 1120 lb of a dark hard wax and about 270 lb of pitch. From the 1120 lb of the dark wax can be obtained 850 lb of a refined cane wax. In addition there can be separated from the crude wax a fatty fraction weighing 480 lb which yields a wide variety of complex compounds that could prove useful industrially. The sterols from the fatty fraction might prove of value in both the vitamin and cosmetic fields.

H. H. Hatt and his associates[98b] in 1950 found that the crude cane wax obtained by extracting the filter cake from the juice clarification with a petroleum solvent, contains much ash-producing material consisting of soaps, phosphatides, and phosphatidates. The crude wax was freed from ash by digesting it with 0.5*N* hydrochloric acid so that the wax had an acid value of 40–45. Its acidic and more volatile components (30–38%) were removed by distillation *in vacuo* at 240–300°C, leaving a residual hard dark wax with an acid value of 4–5.

East Indian Cane Wax. Sugarcane wax is produced as a by-product of the sugar industry at the Ravalgaon Sugar Factory in India. East Indian cane wax has been reported as having a greenish-brown color, and as possessing the following analytical constants: melting point 66–67°C; specific gravity (d^{25}) 0.963–0.984; acid value 12.0–23.4; saponification number 35.5–81.1; iodine number 16.2–31.5; acetyl value 55–60.7; unsaponifiable 62.3–80.0 per cent, Hehner number 83. Crude cane wax, extracted from dry filter press cake by benzene, which is the source of the semirefined wax, has the following constants: melting point 55°C, acid value 24, saponification number 128, iodine number 32, and acetyl value 89[318].

Aswath Narain Rao, and Gupta[13] recommend that the cane wax extracted from the dry press cake by means of a light petroleum solvent be treated with 5 per cent of nitric acid and steam for 20 minutes, cooled, and the separated wax washed free from acid. In this way a pale-yellow tinge is said to be obtained, with a melting point above 60°C. When using petrolic ether ($b_{120\text{-}130°C}$) as the extracting solvent for dry press cake, the yield of crude cane wax is 10 to 15 per cent.

East Indian wax has been reported to contain mixed sterols: *brassicasterol* (m. 148°C, $[\alpha]_D$ −64°C), *stigmasterol*, and *sitosterol*, and the wax from one central contains only stigmasterol, aside from sitosterols.

Argentinan Cane Wax. The cane wax obtained by Cross from filter press cakes in the province of Tucuman, Argentina, was of a greenish color and was much softer than the true cane wax (m. 60–70°C). By fractional crystallization from benzin it was possible to separate the cane wax from the other constituents. The wax so obtained had a melting point of 78–80°C and after further purification and recrystallization it melted at 81–83°C. Suspended substances removed from raw juice by means of a large juice centrifugal yielded a product which upon one crystallization gave a pure, hard wax with a melting point of 82°C.

Brazilian Cane Wax. The crude cane wax obtained from the extraction of press cake in Brazil had a melting point of 79°C, saponification number 83, acid value 6, and iodine number 34.

Australian Cane Wax. The dry muds from the centrals at Mackay, Queensland, have a high wax content (10.7–18.5%) while those from the Bundaberg factories are low (3.6–7.0%) in wax. According to Venton[302], the wax content of different varieties of cane varies considerably. Venton[302] has given a design for a large-scale production plant. He states that benzene and Shell solvents X_2 and X_3 are recommended as solvents, and that acetone and alcohol are inferior. The cost of drying the mud was computed at 16 shillings per ton of dry mud; the drying is conducted at a temperature below the melting point of the wax. The dry mud is ground to a 20 mesh size, and then treated with an equal weight of the solvent. The solvent is receovered by a standard solvent recovery method.

A sugarcane wax process developed by H. H. Hatt and his associates[93b] makes it unnecessary to use solvent for extraction. It is a three-step refining process: demineralization with hydrochloric acid, vacuum distillation to get rid of the components of lower molecular weight, and a chromic acid bleach based on the I. G. Farbenindustrie method for montan wax. The first step, demineralization, takes 24 hours; it is the time-limiting factor in plant design for the new process. The average mineral content of the wax complex is 5 per cent, and it is estimated that 900 gallons of 3.3 per cent hydrochloric acid are needed to treat 1070 gallons of wax per day.

After treatment with hydrochloric acid the wax is sent to the distillation unit where the lower-molecular-weight components are removed under 1 mm pressure and 300°C. Special stainless steel is needed to resist the fatty acids coming over at that temperature; the receiver is heated because the later fraction of the distillate melts at 60°C. Vacuum is obtained by a four-stage steam ejector unit. In the last stage, the remaining wax is bleached at 110°C with a mixture of chromic and sulfuric acids. It is then washed with boiling sulfuric acid (30% weight for volume) and with water.

The washed wax is dried under low (200 mm) vacuum and flaked if desired. The yield of refined cane wax is estimated at 50 per cent. About 4 million tons per year of crude cane wax of Australian wax could be made available, for refining.

The fully refined (bleached) Australian cane wax is pale in color, hard, and glossy, and has an acid value of 130–160[98b]. The high acid value permits modification into a new series of waxes.

Cuban Cane Wax. In 1927 Bardorf[19] reported that the filter press cake on a Cuban estate contained 21.16 per cent of wax, and molasses may contain 2 to 3 per cent. The wax complex consists of at least five different constituents, three extractable by acetone, one by alcohol and one by water, but the most important are an olive-green, soft wax (m. 52°C) extracted by acetone, and a brown wax (m. 82°C) extracted by alcohol. The green wax may be heated to 460°C, just below its boiling point without decomposition. The brown wax is a little less stable, and starts to decompose at its boiling point which is 450°C. The green wax contains 6–7 per cent oil which distills off at 280–300°C (also see Distillation of Cane Wax, p. 225). The saponification numbers of the wax complexes are very high, varying from 168 to 800. The waxes are easily emulsified in water or sugar solution.

In the practical application of these principles today the so-called sugarcane oil, resin, and wax are separated from the crude cane wax by selective solvent extraction. The operation at the Cuban-American Company's big sugar refinery at Centrales Chaparra is to leach by a continuous vertical extractor a crude wax from the wet press cake coming directly from the cane-crushing plant. The extraction is said to use a continuous countercurrent principle employing warm heptane as the solvent. The wax complex is then shipped to Gramarcy, Louisiana, where the crude wax is extracted with acetone at 90–100°C. About 18 per cent of the crude wax—consisting of calcium and magnesium salts of the wax and resin acids—remains undissolved in the hot acetone and is separated out. The hot solution is then cooled to room temperature to crystallize the desirable wax fraction, leaving the remainder of the crude dissolved in the solvent as a fatty oil.

The yields of the components of the Cuban crude cane wax are roughly 35–40 per cent sugarcane oil, 18–20 per cent of resinous matter, and 40–45 per cent of wax. The analytical constants for the brown cane wax (not fully refined) as given by Whyte and Hengeveld[320] are as follows: melting point 79°C, saponification number 120, acid value 27, iodine number 57, and acetyl value 95. The wax can be bleached to a pale tan color, and freed from some of its resinous constituents, by means of a hot mixture of chromic and sulfuric acids.

It has been estimated that 60 million pounds of wax per year can be obtained as a by-product of Cuban sugar cane mills.

West Indies cane wax resembles Louisianan and Australian waxes but differs from South African and Philippine waxes.

Sugarcane oil is composed of crystalline sterols, fatty acids, and an indeterminate residue. It can be made into a lime-grease. Other possible uses are as a source of vitamin D and carotene.

Philippine Cane Wax. A crude cane wax received from the Philippines was brown in color, streaked with a great deal of green material which contained much chlorophyll. Since the behavior of chlorophyll is not too unlike that of fat-wax substances it is not easily separated. Attempts to saponify a portion of the wax led to serious trouble in separating the true wax ingredients from the emulsion. An attempt was then made to destroy the chlorophyll by boiling the crude wax with a 50 per cent solution of sulfuric acid and sodium dichromate. On cooling, the wax separated at the top, whence it was washed with water, taken up in chloroform, and filtered through animal charcoal to yield a soft brown wax[311]. The latter semicrude appeared to be quite identical to the original wax except that chlorophyll, and traces of sugar, minerals, or other soluble matter, were thereby removed. The yield of semicrude wax by this procedure was about 94 per cent.

In another experiment the crude wax was distilled under reduced pressure, producing a pale yellowish wax of soft consistency. These soft waxes appeared to contain in part glycerides of unsaturated and saturated acids. By extraction of the crude wax with warm ethanol, then chilling and siphoning the crystal wax, and repeating the extraction and separation six times, there resulted a refined wax of pale green color and of a high degree of hardness like carnauba wax. Careful treatments with warm (not hot) ethanol removed the chlorophyll rather slowly, but easily removed the free fatty acids and the fats. Hanzely[311] obtained a melting point of 79.4°C (174°F) for the purified product, which confirms that of Cross who gives 78–80°C as the melting point for a true cane wax.

An attempt was made to free Philippines crude wax from chlorophyll, soft vegetable fats, and fatty acids by treatment with hot alcohol, chilling, and centrifuging out the crystals of wax. The product obtained was a pale moss-green colored wax, lustrous, fairly hard (durometer test 80 at 28°C), and brittle. It could be sun bleached. The analytical constants on this semirefined wax were: specific gravity (d^{25}) 0.978, melting point 77.2°C (171°F),

TABLE 49. PHYSICAL CHARACTERISTICS OF PHILIPPINE CANE WAX

	Crude Green Cane Wax	Semicrude Brown Wax
Specific gravity at 25°C	0.998	0.972
Melting point	52–70°C	71.1°C
Acid value	56.8	40.0
Saponification value	137.5	147.5
Iodine number	83.8	45.6

acid value 23.1, saponification number 95.0, and iodine number 19.8. The alcohol treatment, however, removes some of the valuable fatty acid esters of monohydric alcohols.

Javanese Cane Wax. Sugarcane wax has been recovered on a commercial scale in Java. The wax is reported to have a melting point of 60–62°C, an acid value of 47, and a saponification number of 177.

Louisianan Cane Wax. A refined sugarcane wax has been prepared, in a pilot plant operation, from the large amount of accumulated tailings at the sugar centrals in Louisiana. The wax is of a greenish brown color, lustrous in appearance, brittle, and ochre in color when subjected to fluorescent light.

In a pilot plant at Houma, the dry press cake from Oliver filters is made slightly plastic with water, formed into pellets, dried, and extracted with either toluene, benzene, naphtha, or light petrolic spirit, toluene being preferred because of the higher yield of wax. The wax obtained from Louisiana cane using naphtha as a solvent has the following constants: melting point 79°C, acid value 23, saponification number 91, and iodine number 38.

The amount of crude wax from the cake at 22 Louisiana factories varied between 5.3 and 16.3 per cent on the dry cake basis. The extract contained 3.6 to 12.9 per cent of hard wax and 1.8 per cent of fatty substances. In the western districts of the state the yield was 11.3 to 16.3 per cent. The fatty substances and the phytosterols and carotene are removable with acetone. The residual wax can be lightened in color by treatment with an equivalent weight of activated charcoal, whence it may be filtered, freed from acetone, and dried.

This wax has a melting point (ASTM) of 77.7°C, softening point 76.9°C, ball and ring melting point 78.9°C, and solidifying (setting) point 78.2°C. It has a durometer hardness of 98 at 25°, 100 at 4°C. The density at 15°/15° is 0.9969; at 25°/15° 0.9919; and at 100°/15°C. 0.8370[311a]. A specimen of Louisiana cane wax had an acid value 13.0, saponification number 57.0, and iodine number 7.96. The unsaponifiable matter was 17.5 per cent.

In sugarcane wax studies made by Balch and Broeg[18] the wax content of millable cane constituting the 1942 crop from Houma Station varied according to the location of the crushing plants. The average content of crude wax they found to vary between 0.114 and 0.241 per cent. The hard wax was found to constitute 51.0 to 68.6 per cent of the crude wax. In studying the wax removal from sugar cane by milling the average percentages obtained in the crude wax content of mill products, and computing same on the cane basis weight, the results were as follows: crusher juice 0.036 per cent, remaining juices 0.024 per cent, bagasse 0.086 per cent, giving a total crude wax content of 0.146 per cent. The average amount of wax removed by milling was 41 per cent.

The crude wax content of clarification mud press cake for the 1942 season at Houma ranged from 3.67 to 8.13 per cent on samples taken from 12 factories in the Eastern District, with a weighted average of 5.86 per cent. The weighted average on the moisture-free basis is 8.75 per cent. The wax content of the press cake in the Western District proved considerably higher, since samples taken from seven factories showed a crude wax content of 2.53 to 4.10 per cent, with a weighted average of 10.22 per cent, or 13.57 per cent on the moisture-free cake basis.

Balch and Broeg[18] have also found that the removal of fatty matter from crude wax to yield a hard wax may be accomplished in several ways. Two solvents, acetone and 2-butanone (methyl ethyl ketone), were compared critically. The latter solvent is more efficient than acetone in removing the fatty matter and the pigments, but it also has a higher solvent power on wax constituents. About 5 per cent more hard wax remains after the treatment with acetone, regardless of whether the crude wax was originally extracted from the mud press cake with toluene or with petroleum naphtha.

Properties of Sugarcane Wax. The analytical constants of the commercial sugarcane wax as given by the Warwick Wax Company, Long Island City, New York, are as follows: melting point 79–81°C; penetration (100 g/5 sec/25°C) 2 (max.); color brown; acid value 23–28; saponification number 65–77; acetyl value 25; iodine number 17; peroxide number 0; ash 0.004 per cent; specific gravity (d^{25}) 0.9830; refractive index (n_D^{25}) 1.5100; (n_D^{90}) 1.4435. The Fisher-Johns melting point of the commercial U.S. refined wax is 74–75 min., 76 bulk, and 79–81°C max. The color is straw-yellow.

Sugarcane wax is partially soluble in cold alcohol; 5.9 g dissolve in 100 ml U.S.P. ethanol (95%) at 25°C; and it is partially soluble to a much greater extent in hot ethanol. Ten parts of cane wax dissolve in 100 ml of butanol at 57°C, in 100 ml of benzene at 67°C, in 100 ml of ethyl acetate at 44°C, in 100 ml of turpentine at 35°C, and 100 ml of light naphtha at 39°C. Cane wax is partially soluble in ethylene dichloride; 1.6 g dissolve in 100 ml at 37°C. It is quite soluble in chloroform, but very sparingly soluble in cold ether. Hot ethyl ether dissolves it to some extent, depositing small crystal grains on cooling. The wax is soluble in hot amyl alcohol. The highly refined wax is reported as melting at 82°C and solidifying at 80°C and has a specific gravity (d^{10}) of 0.961. When made into a taper it burns with a fine white flame like spermaceti.

The analytical constants of the cane waxes (cerosins) may be fairly well summed up as shown in Table 50.

Chemical Constituents of Cane Wax. A fairly large proportion of the fatty matter (40 per cent) in crude cane wax can be readily saponified. Saponification yields about 45 per cent of fatty acids. According to Mitsui

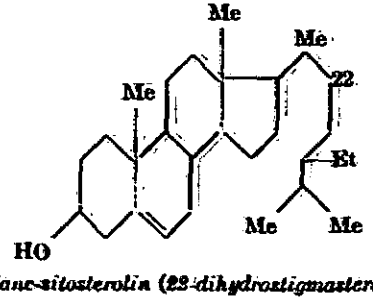
TABLE 50. ANALYTICAL CONSTANTS OF THE CANE WAXES

Grade	Color	M.P. (°C)	Sp. Gr. (d^{25})	Hardness D at 25°C	Acid Value	Sapon. Number	Iodine Number
Crude	olive-green	52–60	0.988–0.998	0	24–57	128–177	32–84
Semirefined	green-brown	61–71	0.972–0.978	50–85	14–47	54–148	19–40
Louisianan	light brown	78	0.991–0.999	98	13	57	8
Double-refined	dull yellow	77–82	0.961–0.979	85–96	8–23	55–95	13–29

and Matsuda[130c], the fatty acids are composed of 1.3 per cent volatile acid (*caproic acid*); 20 per cent nonvolatile acids which are soluble in sodium bicarbonate (resin acids); and 78 per cent nonvolatile acids which are insoluble in sodium bicarbonate. The latter acids are composed of 28 per cent liquid acids (*α-linolenic*, 0.3; *α-linoleic*, 4; and *oleic*, 14), and 50 per cent of solid acids (*capric*, trace; *myristic*, 0.8; *palmitic*, 38; *stearic*, 4; *behenic*, 1.5; and others).

The unsaponifiable matter consists of about 80 per cent of the higher alcohols, such as *ceryl* and *myricyl alcohols*; about 10 per cent of a mixture of *sterols*, from which *brassica-*, *stigma-*, and *sitosterols* have been isolated; and about 5 per cent of ketones, principally *pentatriacontanone*.

Sterols in Cane Wax. Mitsui[131] reported in 1937 that on extraction with benzene or ether, the press cake from the manufacture of raw sugar yielded 8.3 per cent of wax; that from the manufacture of white sugar yielded 2 per cent; and bagasse 0.43 per cent. From 100 kg of the wax from the press cake could be obtained 2.0 kg of *stigmasterol* and 0.77 kg of *sitosterol*, $C_{29}H_{49}(OH)$. These were isolated in the tetrabromide and acetyl derivatives. In 1938 the same investigator extracted the unsaponifiable matter with acetone, and removed the precipitate formed on cooling. Light yellow plates were obtained from the filtrate, and were identified as *stigmasterol*. *Sitosterolin* was also isolated from the filtrate.



Cane-sitosterolin (22-dihydrostigmasterol)

In 1939 Mitsui[131] removed the crystalline substances from cane wax with acetone, and extracted from the unsaponifiable a reddish-brown oil

by treatment with cold methanol. By treatment of this extract with benzene a crystalline product (m. 206°C) was obtained, and this had the formula $C_{29}H_{52}O_2$. It was named *α-saccharostanediol.* The yield was computed as 4 per cent of the wax. The mother liquor of α-saccharostanediol was kept at 0°C and saturated with HCN. Sitosterol allophanate crystallized out. By treating the filtrate of the latter with acetone and methanol, colorless scales (m. 160°C) were obtained. The substance is named β-saccharostenone and has the formula $C_{29}H_{48}O$. The yield was 0.1–0.2 per cent of the wax.

Chemical Composition of Semirefined Cane Wax. The chemical composition of a semirefined sugarcane wax based upon its chemical constants is given in Table 51.

Uses of Sugarcane Wax. As early as 1914 sugarcane wax was known to be useful as a partial substitute for beeswax in the stout, dark-colored candles of the Russian Orthodox churches. In 1918 Rindl[231] referred to its use to a limited extent in the polish and electrical industries; for gramophone records; and as a replacement wax in general for carnauba, beeswax, and montan wax in other industries. According to Crowe, samples of American wax of 174°F melting point were sent to the trade, and the response indicated that there would be a good demand for the product whenever produced in quantity. Crowe stated that it can be used in the

TABLE 51. CHEMICAL COMPOSITION OF SEMIREFINED SUGARCANE WAX

Wax Esters:	78–82 per cent
Myricyl palmitate (m. 73°C), 28%	
Ceryl melissate (m. 86–87°C), 1–2%	
Myricyl melissate, small amount	
Phytosterol esters of dihydroxypalmitic acid (m. 55°C), 13%	
Stigmasteryl ester of palmitic acid, 37–38%	
Glycerides: present, small amount	
Free Fatty and Wax Acids:	14 per cent
Palmitic acid, large amount	
Melissic acid, small amount	
Hypogaeic acid (m. 21°C), small amount	
Alcohols:	6–7 per cent
Aliphatic (free) trace	
Cyclic and derivatives:	
Brassicasterol, $C_{28}H_{46}O$ (m. 138°C), 0.8%	
α-Saccharostandiol, $C_{29}H_{52}O$ (m. 206°C), 4%	
β-Saccharostenone, $C_{29}H_{46}O$ (m. 106°C), 1½–2%	
Hydrocarbons:	3–5 per cent
Hentriacontane (m. 68°C)	
Pentatriacontane (m. 75°C), 1½–2%	
Mineral Matter:	½–1 per cent

Note: The above composition is based on a wax of 67°C melting point having an acid value 25, saponification number 80, ester value 55, and an iodine number of 29. The unsaponifiable amounts to 62.3 per cent. Mineral matter contains Ca, Mg, Al, Fe and P_2O_5. The highly refined sugarcane wax contains less of the sterol esters.

manufacture of polishes, molded articles, and impregnated and coated products, and to replace vegetable waxes now difficult to secure.

Most of the above uses have been realized, and numerous others added. The exploitation of sugarcane wax has been aided by the recent advances made in the refining so that the wax now marketed is practically free from resin and oil, of a paler color, of higher melting point, and of greater hardness.

Waxes of Reed Grasses

Esparto Wax

Esparto wax is derived from a grayish-green grass, called esparto needle-grass, less ornamental than feathergrass of gardens, and is indigenous to south Spain and North Africa, where it is known as Alfa. Its botanical name is *Stipa tenacissima* L. Another grass, espartograss of the same family, *Gramineæ*, is *Lygeum spartium* L. This grass has stiff rush-like leaves and grows in rocky soil on the high plains of the Mediterranean countries, especially Spain and Algeria, and is also a source of esparto. The esparto grasses take years to mature, and eventually attain a height of 3 or 4 feet. Because of its toughness esparto has been used in Spain for making ship cables, sandals, baskets, mats, etc. In France, Italy, Spain and Great Britain esparto is used in papermaking.

For papermaking the leaves, 6 inches or more in length, are gathered before they are quite matured, and are harvested during the dry summer months. Without further drying, the esparto of Libya, or elsewhere in the Mediterranean region, is shipped to Scotland where it is dewaxed so that it can be made into paper. Many of the fine grades of paper in the British Isles are made from esparto. Recovery of the wax from the grass was first made by the Tullie Russell & Company, Ltd., in 1909–1910 under a process patented by Cross and Russell[62]. The patentees describe an apparatus by which the broken grass and fine dust are withdrawn from the "willow" by a single, powerful fan, thus keeping the "grass-duster house" clean; the waste passes through two cyclone separators, one of which collects the broken grass and coarse fibers and the other the fine dust, packing them separately and automatically in bags. The entire system is enclosed and the only attention required is the periodical removal and replacement of bags.

The dust is then extracted by percolation with petrolic ether, on the principle of the Soxhlet extractor, the spirit being boiled afterwards in a kettle and recoverd for reuse, leaving the pure molten wax which is run off into molds to cool and solidify. The wax recovery system enables the various esparto paper mills to send their accumulated dustings flailed from the grass to a central plant. The Russell plant thus became practically

the sole world producer of esparto wax. Each ton of grass yields 5 to 7 pounds of fine dust, from which can be extracted 30 to 40 per cent of wax. Each ton of the esparto or Alfa grass will produce on the average 3 pounds of the esparto wax of commerce.

Esparto wax has the following analytical characteristics: specific gravity (d_4^{12}) 0.9891, (d_4^{15}) 0.9880, (d_4^{98}) 0.8370; coefficient of cubical expansion 0.000609 at 25°C; melting point (drop) 78.1°C; setting point 68.8°C; liquating point 65.6°C; Fisher-Johns melting point 69°C min., 72.5°C bulk, 81°C max.; acid value 23.9; saponification number 69.8; mineral matter 0.6 per cent. The solubility of esparto wax in ethanol is 0.244 gram in 100 ml at 25°C, and in ethylene chloride 1.48 grams in 100 ml at 37°C.

Lüdecke[168] investigated the possibilities of the recovery of wax from the offal of esparto grass utilized in Spain and Italy in the preparation of paper pulp. He reported that benzin extraction of the offal yields up to 30 per cent of wax having the following constants: melting point 67.5°C, acid value 22.7, saponification number 79.3, iodine number 22.2, and unsaponifiable 22.3 per cent. The organic solvent which proved best for extraction of esparto was trichlorethylene, $CHCl:CCl_2$. A solvent fractionation of the extracted wax with 80 per cent ethanol yielded 11.7 per cent of a wax-fat mixture, 69.7 per cent of pure wax (acid value 36.03, saponification value 80.38), and 20.4 per cent of bituminous waxy substance.

Esparto wax is chemically composed of esters, sterols, resinols, hydrocarbons, and free acids. It contains 63–65% hydrocarbons. The combined acids include *cerotic, montanic, melissic*(c), and *lacceroic*, principally the latter two and also hydroxy acids. It is also likely that the alcohols of the esters are within the C_{26} to C_{32} range. The principal hydrocarbon is *hentriacontane* ($C_{31}H_{64}$, m. 68°C). A large part of the free acids are resin acids.

Esparto wax is a hard tough wax. It gives a penetration reading of 1.5 at 25°C, which indicates that it is not quite as hard as carnauba wax. It does provide a suitable economic substitute for a part of the carnauba wax component in floor polishes, furniture polishes, and shoe pastes. It blends well with other waxes.

The amount of esparto wax available for sale is somewhat over 500,000 pounds per year, most of this is being consumed in the British Isles in the arts and industries. Normally the price of esparto wax is in the vicinity of twenty-five cents per pound.

Wax of Reed

The common reed, *Phragmites communis*, contains a wax. At the University of Arizona, Tuscon[145], the plant was dried and extracted with petrolic ether; the crude wax so extracted was then separated into wax and nonwax fractions with acetone.

Fiber Wax

"Fiber wax" is a commercial designation given to a wax which has been reclaimed from the straw or other waste material from mills where fibers of grasses or reeds are utilized. Since the source of the the fiber source varies, and is seldom disclosed by the vendor, much uncertainty arises as to its derivation or composition. Some of the lighter colored grades are occasionally adulterated with paraffine, and darker ones with montan wax.

In melting point, fiber waxes range from 61° to 80.5°C (142° to 177°F). In color they range from a yellowish brown, through brown, to very dark brown. The darkest grades are usually the harder and higher in melting point. For example, a specimen of a dark-brown fiber wax had a melting point of 80.5°C, a durometer hardness of 100 at 25°C, an acid value 10.6, saponification number 67.2, ester value 56.6, and iodine number (Hanus) 11.4. This fiber wax closely resembled esparto wax in its general characteristics, and may have been produced from the offal of Spanish or Alfa grass.

The range of constants usually given by commercial sources for fiber waxes is as follows: specific gravity (d_4^{15}) 0.9680–0.9890; m.p. 61–79°C; acid value 16–34; saponification number 61–79; iodine number 11–23.

The addition of 2 per cent of fiber wax (80.5°C m.p.) to paraffine raises the dry melting point from 54.4 to 57.7°C (130° to 136°F), and the addition of 5 per cent raises it to 75.5°C (168°F).

Fiber wax is used in the manufacture of floor polishes and shoe creams; also as a blending agent to produce high-melting-point artificial ceresin waxes. In paste polishes fiber wax gives less shrinkage on contraction than does carnauba wax, and can be advantageously used to partially replace the latter. Fiber wax is compatible with other waxes in almost all proportions.

Glyceria Wax

A wax which resembles carnauba is obtainable from the stems of Australian canegrass, *Glyceria ramigera*. It has a melting point about the same as commercial "fiber wax," namely 82°C. It has the following characteristics: acid value 54.2, saponification number 89.4 (of the ether-insoluble portion), and an ester value 35.1 (of the esters). The wax is insoluble in water. It is slightly soluble in a mixture of ethanol and benzene, in acetone, and in chloroform in the cold, but dissolves freely when boiled in these solvents. The part insoluble in cold ether will not dissolve with boiling. The ether-soluble portion has a specific gravity (d^{18}) of 0.975; the insoluble portion has a specific gravity of (d^{19}) of 0.9819.

Waxes of Sedges

The members of the sedge family, plant order *Cyperaceae*, are herbaceous plants, with three-angled solid stems, bearing alternate three-ranked leaves,

with entire sheaths. There are only a few genera but about two thousand species of sedge. Only the peats derived from sedges yield appreciable amounts of wax. These sedges include cottongrass, *Eriophorum vaginatum* L.; bulrush, *Scirpus lacustris* L.; and probably papyrus, *Cyperus papyrus* L., known as the bulrush of Egypt.

The leaves and flowers of sand sedge, *Carex arenaria* L., have been found to contain 0.50 and 1.50 per cent of wax respectively. These lipid waxes contain *ceryl alcohol* and *carotenoids* (β-carotene). Sand sedge may be found in the sand of the upper part of the beach of Chesapeake Bay, in Northhampton County.

Waxes of Forage Grasses

There are over a hundred species of grasses, natural order Gramineae, which provide the bulk of forage. Wax-containing forage grasses include cocksfoot, perennial rye, lucerne, crimson clover, etc. The waxes are lipid waxes; leaf blades of this kind contain higher aliphatic alcohols, fatty acids, ketones, steroids, hydrocarbons, and glycerides. The waxes extractable from these blades are exceedingly small in amount.

Orchardgrass (cocksfoot), *Dactylis glomerate* L., which is common in the United States, Canada and Europe, is reported by Pollard, Chibnall, and Piper[310] to yield a wax, which consists largely of *n-hexacosanol* ($C_{26}H_{55}OH$, m. 79.5°C), and less than 1 per cent of *tetracosanol* Perennial ryegrass, *Lolium perenne*, has *hexacosanol* as a constituent. *Hexacosanol* is also a constituent of the lipids of bentgrass, *Agrostis alba* L., a native of Europe, and known in the British Isles and America as redtop. For wax of crimson clover, *Trifolium incarnatum*, see p. 319.

The lucerne leaf, *Medicago sativa* L., family order Papilionaceae, commonly known as "alfalfa," strictly speaking is not a grass. It yields a wax containing *n-triacontanol* ($C_{30}H_{61}OH$, m. 86.5°C) and *myristone* (m. 74–75°C). Myristone constitutes 0.17 per cent of the dry blade. Alfalfa seed yields a mixture of glycerides of palmitic, stearic and oleic acids, but no wax. β-amyrin is found in both blade and seed.

Lacryma Wax

A wax is found in the stems of the *Coix lacrymajobi* (*C. lacryma* L.), a grass with a bony fruit. The plant is indigenous to the East Indies and Japan. The bony white seed are called "Job's tears." They have some value as a medicine, and are used in China as a food. They are sometimes made into necklaces. The wax is said to be similar to esparto wax.

Waxes of Cereal Grasses

The cereals, which broadly speaking are a part of the grass family, are barley, *Hordeum vulgare*; buckwheat, *Fagopyrum* sp.; corn, *Zea mays*;

flax, *Linum usitatissimum*; oat, *Avenia* spp.; proso (broomcorn), *Panicum miliaceum*; rice, *Oryza sativa*; rye, *Secale cereale*; sorghum, *Sorghum vulgare*; and wheat, *Triticum* spp. All cereal blades contain waxes, and some in sufficient quantity or availability to be economically recovered.

The whole seed of certain varieties of corn, *Zea mays* L., when extracted with the proper solvent yields a minute amount of wax, the characteristics of which have been described (see p. 307). A lipid wax has been extracted from the pollen of Japanese white flint corn, *Zea indurata* (see p. 308). A lipid wax has been isolated from the oil pressed from Koryan corn of Manchukuo (see p. 308).

Wax in minute amount has been recovered from the oil pressed from common flax, *Linum usitatissimum* L. (see p. 201). Both bran and polishings of rice, *Oryza sativa* L., contain sufficient wax to make its recovery economical (see Rice bran wax). Certain varieties of sorghum, *Sorghum vulgare* Persoon, contain wax, which is recoverable as a by-product in the milling of the grain in the production of grits (see Sorghum-grain wax).

The wax of the wheat blade, *Triticum aestivum* L., is reported to contain a lipid wax. The wax contains a wax alcohol, namely *n-octacosanol* ($C_{28}H_{57}OH$, m. 83.4°C), together with wax acids, a hydrocarbon (m. 66°C), and steroids.

Straw from cereal grains yields 1.8 per cent of a dark-green lipid wax when extracted with petrolic ether. This soft crude wax can be refined with activated carbon to produce a light-yellow wax of a higher melting point (66.5°C?), with a yield of 85.2 per cent. Cellulose prepared from the wax-extracted straw will bleach more readily.

Sorghum-Grain Wax. *Sorghum vulgare* (*Andropogan sorghum* Botero) is a large grass of many varieties, cultivated throughout Africa and grown extensively also in India, China, Manchuria, and the United States. In the United States sorghums are grown from the Gulf of Mexico to South Dakota. Broomcorn is a variety grown mostly for forage and grain, and to a lesser extent for silage, broomcorn and sirup. The hulls of broomcorn, particularly a grain like Western Blackhull kafir, yield a wax about as hard as carnauba. The wax can be removed by extracting the whole seed or unground grain with hot solvent (e.g., "Skellysolve B").

Kurtz, Jr.[140] investigated the wax yield in old plants and reported that a variety of sorghum known as johnsongrass, *Sorghum halepense* L., contained but 0.04 per cent of wax. Kummerow[143] states that varieties of *Sorghum vulgare* contain about fifty times more wax and two-thirds as much oil as yellow corn. The average yield is 0.32 per cent wax and 2.75 per cent oil.

Varieties of sorghum grain are milo, kafir, durra, feterita, kaoliang, and shallu. Milo and kafir are of the greatest interest in the United States,

since they yield starch, wax, oil, grits, oil meal, and bran. According to Isely[116] the wax has been recovered as a by-product from milo, by the Dodge City Industries, Inc., Dodge City, Kansas. The plant at Dodge City merely wet-mills the milo into usable components, principally grits for which there is a ready market, and the bran is shipped to Kansas State College, for the recovery of the wax. A 100-pound sack of bran yields about the same quantity of wax as is obtained in a year from one 40-foot palm tree. The wax resembles carnauba.

Bunger and Kummerow[43] have extracted the wax from the whole grain of four varieties of sorghum, namely, Standard Blackhull, Westland, Cody, and Sunrise. They reported that if the wax is extracted by refluxing on a steam cone with "Skellysolve B," the hot extract filtered, cooled to 0°C, and the precipitate removed with the aid of a Buchner funnel, 0.25 per cent of a very hard wax is obtained. The bran from the Cody variety when extracted in a Soxhlet extractor with the same solvent yielded 6 per cent of crude wax, which could be purified by recrystallization from a mixed solvent of "Skellysolve B" and acetone, with a yield of 80–85 per cent for the varieties tested.

The chemical properties of sorghum waxes have been given by Bunger and Kummerow (Table 52).

Chemical Composition. The chemical composition of sorghum grain wax is not yet fully known. It appears to be comprised of about 46 per cent of esters—inclusive of hydroxy and multiple esters, 9 per cent of free fatty acids, and 44 per cent of hydrocarbons and other unsaponifiables. The esters are compounds of C_{28}–C_{30} alcohols with C_{30}–C_{24} acids.

According to Bunger and Kummerow[43] the acids (m. 71–77°C) in the hydrolyzate of Sunrise sorghum wax amount to 36 per cent. The melting point would be consistent with that of a mixture of monoethanoid acids in the range of C_{20}–C_{24}, although the melting point could be influenced by the presence of hydroxy monoethenoid acids which might be as high as 20–21 per cent on the basis of appreciably high acetyl and iodine numbers

TABLE 52. CHEMICAL PROPERTIES OF SORGHUM WAXES

	Standard Blackhull	Westland	Cody	Sunrise
Acetyl number	53.3	55.1 ± 2.8	44.3 ± 3.5	62.9 ± 4.4
Acid number	10.05 ± 0.61	13.8 ± 0.83	16.2 ± 1.85	13.51 ± 0.55
Sapon. number	16	20	44	25
Ester number	6	6	28	11
Iodine number (Wijs)	19.35 ± 0.87	20.88 ± 0.40	15.66 ± 0.87	15.69 ± 1.63
Melting range (°C)	77–80	77–82		79–82

obtained. Yamomoto and Ninomiya[325] in 1936 isolated *arachidic acid* (m. 76°C), but made no reference to the presence of other acids. Bunger[43] calculated the amount of free acids as 9 per cent on the basis of a molecular weight of 368 (C_{24} acid, namely *tetracosanoic*). The C_{22} acid may be either *behenic* (m. 81°C) or *isobehenic acid* (m. 76°C).

Yamamoto and Ninomiya[325] isolated *ceryl alcohol* (m. 80°C) and an unknown alcohol (m. 83–84°C) presumably *myricyl alcohol*. Hence simple esters in the wax would consist of *ceryl arachidate* (hexacosanyl cicosanoate, m. 72–73°C) with a molecular weight of 677.20 and others of still higher molecular weight. These investigators report the presence of 19 per cent of the eicosanoic ester, but a large proportion of what they considered to be free alcohols ostensibly are components of diesters, and triesters. The ester values of the sorghum waxes are far lower than can be accounted for in calculating the esters as either "simple" or "simple hydroxylated" esters.

Yamamoto and his co-worker[325] were the first to isolate so-called hydrocarbons from the petrolic-ether insoluble extract of the testa (outer covering of the seed) of Kaoliang grains. The hydrocarbons melted at 78–79°C. Bunger and Kummerow[43] 17 years later reported the melting range of the hydrocarbons of Westland sorghum wax to be 75–83°C, corresponding ostensibly to hydrocarbons in the range of C_{36}–C_{42}. The hydrogen analysis of the hydrocarbon fraction gave 83.8 per cent, H 13.8 per cent, discounting the presence of such high-molecular-weight hydrocarbons, and indicating to these investigators the presence of an oxygen-bearing substance, e.g., a ketone *with* a molecular weight of about 670 as a principal constituent of the unsaponifiable. Generally speaking, vegetable waxes ordinarily contain C_{31} hydrocarbon (m. 68°C) or homologs close to C_{31}. Hence the high melting point of the unsaponifiables must be due to the presence of high-melting ketones or other substances, and the hydrocarbons actually only a few per cent.

Although the physical characteristics of sorghum waxes are quite similar to those of carnauba wax, the latter has a very much higher ester value.

Bunger and his co-worker[43] compared four methods for the separation of unsaponifiables from both carnauba and sorghum grain waxes. The lowest value of unsaponifiables in the hydrolyzate for carnauba wax was 54 per cent by the Zweig and Taub procedure, and the highest value, 60 per cent, was obtained by a modified Koonce and Brown method. On Westland sorghum wax the Zweig and Taub procedure gave 67 per cent, whereas the modified Koonce and Brown method gave 78 per cent.

Alfalfa Wax. The lucerne leaf, *Medicago sativa* L., commonly known as "alfalfa," yields a wax of high melting point. Blair and associates[30b] obtained a free alcohol (m. 85–85.5°C) which they believed to be a mixture of *n-octacosanol* and *n-triacontanol*, $C_{30}H_{61}OH$ (m. 86.5°C), the latter predomi-

nating. A so-called carotene fraction contained primarily paraffins (m. 66.5–67°C), a mixture of *nonacosane* and *hentriacontane*, and also fatty acid esters of the C_{28} and C_{30} alcohols. *Myristone* (m. 74–75°C) and *n*-triacontanol were previously reported as components, the myristone constituting 0.17 per cent of the dry blade. The chief ester is probably *myricyl palmitate*. Alfalfa seed yields a mixture of glycerides of palmitic, margaric, and stearic acids, but no wax. β-amyrin is found in both leaves and seed.

Ricebran Wax. Both bran and bran coats obtained in the milling of rice, *Oryza sativa* L., family Gramineae, contain a lipid wax. Rice bran contains 15 to 18 per cent and rice polishings 20 per cent of oil[269]. The commercial yield (of edible rice oil) is, however, more like 5 to 7 per cent, varying with the temperature at which the extraction is made, the solvent used, source and history of the bran, and other factors. The yield of wax, if recovered from the crude rice oil, is somewhat less than 2 per cent, or less than 0.4 per cent on the bran basis.

Oil from rice bran has now become an edible oil of commercial value; hence ricebran wax may become of importance as a by-product. Solvent-extracted from the freshly milled rice bran, the oil is low in free fatty acid. It can be converted by conventional refining and bleaching procedures into a clear, light-colored product having a good flavor. The bran from which the oil has been extracted is bagged and sold as an animal feed. The Houston, Texas, plant of the Wonder Rice Oil Company is one of two plants in the United States for the continuous solvent extraction of oil from rice bran. The other plant is that of the American Rice Growers Cooperative Association, also in Houston. The capacity of the Wonder plant is 100 tons tons of bran per day and 30,000 pounds of semirefined oil. Hexane is ordinarily used as the extracting solvent and extraction of the bran is conduced on the countercurrent principle[60a].

Rice oil commercially produced from the offal in the milling of rice may be dewaxed—before refining with acid and alkali—by the use of a DeLaval separator and basket centrifuge. The oil can also be dewaxed by the use of evacuated, unglazed porcelain cylinders covered with a filter cloth. A good yield is obtained at 20–25°C with suction at 50 mm Hg pressure. However, the studies of Cousins and his coworkers[60a] of rice-bran wax have been made on the tank settlings from crude rice-bran oil.

The crude wax containing glycerides may be separated from crude rice oil by wintering at 20–25°C, and then treated with a solvent such as 5 per cent methanol in commercial *n*-hexane, to effect a sharp separation of soluble and insoluble parts. Without the use of solvent the wax from the tank settlings cannot be effectively separated by filtration methods. At the Southern Regional Research Laboratory, New Orleans, La., Cousins and his co-workers[60a] made a particular study of the use of acetone, and

of isopropanol as extracting solvents for tank settlings. They state that the yield of wax varies with the temperature at which the extraction is made, the solvent used, the source and history of the bran, and several other factors. Yields varying from 3 to 9 per cent on the total basis have been reported.

These investigators employed a batch of tank settlings (S-1) provided by a leading commercial processor of rice oil. The settlings were of light-brown color, and possessed a good odor; they were 96.4 per cent soluble in hot hexane. However, they also used tank settlings (S-2) which were dark brown in color, of a charred organic odor, and only 79.5 per cent soluble in hot hexane. Before each portion of settlings was used, it was melted and filtered through a 60-mesh sieve to remove any coarse trash.

The analysis of tank settlings (S-1) gave: iodine number 77.0, free fatty acids (as oleic) 21.6 per cent, volatiles 4.1 per cent, saponification value 166.7, unsaponifiable 14.0 per cent, phosphorous 0.44 per cent. Tank settlings (S-2) gave: iodine number 71.8, free fatty acids 6.5 per cent, volatiles 6.5 per cent, saponification value 179.8, unsaponifiable 10.3 per cent, and phosphorous 1.64 per cent.

In the preparation of the "acetone-insoluble fraction" which contains the lipid wax, one part of acetone was mixed with one part of tank settlings, and the mixture filtered under vacuum. The mixing with acetone and filtration were repeated twice, using half of the allotted acetone each time. The acetone-insoluble or wax fraction then was air-dried for 48 hours. The dried product was a tan-colored powder slightly tacky to the touch. In weight it amounted to 23.8 per cent of the tank settlings (S-1) used in its preparation.

The crude lipid wax has an iodine number 29.6, free fatty acids 10.7 per cent, volatiles 3.3 per cent, unsaponifiable 44.8 per cent, and phosphatide (as phosphorous) 0.79 per cent.

Ishiwata[116a] refers to "crude rice wax" as having an acid value of 8 and a saponification number of 90. After treating the crude rice wax with chromic and sulfuric acids and washing the treated wax he obtained a light-colored wax with a melting point of 80–82°C, acid value 17, saponification number 90, and iodine number 4. Another Japanese investigator, Kitsuta, claims to get pure rice wax by extracting rice polishings (20% oil) with benzene to remove the oil, concentrating the extract, and filtering off the wax which when washed with solvent leaves a wax of 80°C melting point, iodine number 8. It is stated that 71 kg of pure rice wax can be obtained from 900 kg of polishings.

Refined Ricebran Wax. Cousins and associates[60a] have employed various methods of refining ricebran wax, and have given the analytical constants for the refined product and compared it with carnauba wax. The yield of

TABLE 53. ANALYTICAL CONSTANTS OF REFINED BRAN WAX AND CARNAUBA WAX

	Refined Rice-Bran Wax	Carnauba Wax
% Free fatty acids	2.1–7.3, av. 3.8	2.9
Iodine number	11.1–19.4, av. 15.2	9.4
% Unsaponifiable	55.1–67.0, av. 58.1	56.9
Saponification number	56.9–104.4, av. 80.7	77.0
% Phosphorous	0.01–0.18, av. 0.09	0.00
% Volatile matter	0.38–2.94, av. 0.94	0.25
Melting point (drop), °C	75.3–79.9, av. 77.9	83.4
Softening point, °C	74.3–79.0, av. 76.5	82.5
Hardness by durometer	av. 100	100

refined wax varied from 3.4 to 13.7 per cent on six samples differently prepared. The analytical constants are given in Table 53.

These investigators find that isopropanol is an ideal solvent for isolating a hard wax from tank settlings, since it is a poor solvent for the hard wax fraction, but a reasonably good solvent when used hot, and its boiling point is just above the melting point of the wax, yet low enough to permit easy removal from wax and oil. Hexane and heptane are inferior to isopropanol or butand as solvents for wax purification.

Japanese Practice. In cage-pressing rice polishings, the preheating treatment is best done when the product contains about 8 per cent of moisture, and at a temperature of 90°C for 3 to 4 minutes at low pressure, then at high pressure for 12 to 15 minutes[199]. Rice polishings, containing 7.5–8.5 per cent moisture and 20 per cent total oil, when treated with solvent (1 liter/100 grams) at 30 to 50°C for 10 minutes yielded 19 per cent of crude oil[269]. Tsuchiya[279] reported the analyses of 23 samples of crude rice oils: specific gravity (d^{30}) 0.912–0.918, refractive index (n_D^{30}) 14664-1.4708, saponification number 179–187, unsaponifiable 3.6–5.0, and ash 0.13–0.72 per cent. The ash content is reduced to below 0.01 per cent by refining; the dewaxed rice oil still contains an appreciable amount of unsaponifiable substance.

Crude ricebran wax obtained from dewaxing rice oil has according to Tsuchiya[279] an acid value 34.1, a saponification number 174.8, and an iodine number 51.6. It is a soft wax and contains only a small proportion of a highly valued wax constituent, separable by repeated washings of the crude wax with methanol and then with acetone. The hard wax residuum (refined wax) melts at 74–75°C, has an acid value 14.8, saponification number 79.5, iodine number 59.7, and unsaponifiable 31.7 per cent. If further purified by washing the wax with ether and then with chloroform, a hard pure wax is obtained which melts at 75–76°C and has a saponification number 72.8, iodine number 12.6, and unsaponifiable 48.7 per cent. One kilogram of crude rice-oil yields 180 grams of crude wax but only 10 grams of the wax with the 74–75°C melting point. Hence Tsuchiya[279] states it to

be more practicable to hydrogenate the crude rice-oil wax, to secure an adequate economic yield for utilization in the industries.

Bleached Ricebran Wax. At the Southern Regional Laboratory, New Orleans, the refined ricebran wax produced from tank settlings was bleached from a dark to a tan color by means of hydrogen peroxide and then further bleached to a pure white color by means of chromium trioxide (CrO_3) and sulfuric acid (H_2SO_4).

The ordinary refined bran wax is practically black in color when liquid. It will not respond to activated clay or carbon as decolorizing agents. It will respond to hydrogen perioxide (H_2O_2), and a combination of H_2O_2, CrO_3, and H_2SO_4, as discovered by Ueno and his co-workers[286], and give a practically white wax.

In a typical bleaching with chromium trioxide, 1 part of sample was mixed with 4.5 parts of 40 per cent sulfuric acid. While the mixture was at 95°C, 0.5 part of CrO_3 was added slowly and with constant stirring. Heating and stirring were continued for a period of 2.5 hours, and then the sample was washed successively with 40 per cent sulfuric acid and distilled water. The Gardner color of the bleached melted sample was 4. Employing 1 part instead of 0.5 part of CrO_3 produced a color of 1. The Gardner color (10) of wax bleached (with peroxide with) the chromium trioxide is 18 in the liquid state.

When a combination of hydrogen peroxide and chromium trioxide (generally 0.5 part of 29 per cent H_2O_2 and 1 part of CrO_3 per part of wax) was used the bleaching action produced a white wax. In such a bleaching the H_2O_2 and 40 per cent H_2SO_4 were added first and mixed for about one hour at 95°C before the CrO_3 was added slowly. The spent bleaching reagents were removed by washing the wax successively with a solution of sulfuric acid and water.

Chemical Composition of Ricebran Wax. The chemical composition of ricebran wax comprises esters of waxy acids of 22, 24, and 26 carbons, combined with alcohols of 26, 28, and 30 carbons. It also contains small amounts of wax acids of 28, 30, and 32 carbons. The softer constituents contain both saturated and unsaturated acids of the range C_{14}–C_{20}. The wax also contains sterols.

The principal alcohol constituent is *myricyl alcohol* (m. 85°C), isolated by Nabenhauer and Anderson[197] from the unsaponifiable recovered from the oil extracted from rice bran with petrolic ether. Yamazaki and Ogawa[327] have estimated the melissyl (myricyl?) alcohol content of the unsaponifiable as 45 per cent. The balance of alcohols appears to consist principally of ceryl alcohols, both normal and iso. These latter investigators report ceryl alcohol 22, and *ibotaceryl* (isoceryl) *alcohol* 10 per cent in the unsaponifiable, leaving 20 per cent of unidentified material. Ueno and his

co-workers[287] have also reported myricyl alcohol and a smaller amount of ceryl alcohol as the chief constituents of the unsaponifiable. They also confirmed the presence of *sitosterol* and *stigmasterol*.

The crystalline portion of the unsaponifiable was found by Nabenhauer and Anderson[197] to contain both *dihydrositosterol* (m. 144–145°C, $[\alpha]_D$ 24°), and *stigmasterol* (m. 169–170°C, $[\alpha]_D$ −50°). By extracting rice bran with ethyl ether Weinhagen[314] obtained from the solid portion of the extractive 4.7 per cent of phytosterols and 90.6 per cent of fatty acids, substantially pure *palmitic acid*.

Tsuchiya[279] reported that the hard portion of ricebran wax consists mainly of an ester of tetracosanoic acid and myricyl alcohol; Tange[270], however, has attempted to prove that the myricyl alcohol exists in the form of *myricyl cerotate*, which would seem quite plausible because of its higher melting point, in relation to that of the wax. The hard wax would then contain 43–44 per cent of *myricyl cerotate*, 21–22 per cent of *ceryl cerotate*, and about 9.5–10.5 per cent of *isoceryl-isocerotate*. Ricebran wax contains 6.5–7.5 per cent of free fat acid, presumably *palmitic acid*, and a small amount of *oleic acid*. A portion of the palmitic acid is believed to be combined with the phytosterols.

Ricebran wax contains no glycerides, and only a trace of *phospholipides* and *squalene*, and *tocopherone*. Squalene, a highly unsaturated hydrocarbon, is contained in rice oil to the extent of 332 mg per 100 g of oil. Ueno and associates[286] report the presence of palmitic, oleic, linoleic, and a small amount of stearic acid in ricebran wax. They believe that the unsaturated acids may exist as mixed glycerides with acids of high molecular weight. They also report the presence of either a C_{24}- or C_{26}-unsaturated alcohol and a saturated acid, $C_{31}H_{62}O_2$.

Uses of Ricebran Wax. It has been suggested that ricebran wax be used as the wax constituent of chocolate enrobers, as an enteric coating for lozenges, as a constituent in wax emulsions used in the treatment of fruit and vegetables, as a partial carnauba replacement in polish emulsions, and as an ingredient in the foundation employed in the manufacture of carbon papers. The white wax, which has a degree of lubricity, would find use in cosmetics, inclusive of lipstick.

Hydrogenated Rice Wax. The wax produced from the lipid material filtered from rice oil in Japan and then hydrogenated is referred to in the literature as rice wax (instead of ricebran wax).

Tsutsumi[283] reported that rice oil having an acid value of 158 and an iodine number of 113 when hydrogenated at 180°C with an initial hydrogenation of 15 atmospheres for 1½ hours, with a 2 per cent nickel oxide, and 3 per cent acid clay as catalyser, gave a hydrogenated product having an iodine number of 2.0 and an acid value 157.3. The presence of 1¼ to 1½ per cent

of water is helpful only when hydrogenating rice wax because of its lower acid number.

Ueno and his co-workers[288] found that when 30 parts of pure stearyl α-, or β-naphthylamide was added to 100 parts of hydrogenated rice wax, a hard wax with a 72–83°C melting point was obtained. This modified wax made a good substitute for carnauba wax in its utilization for polishes.

Waxes of Bamboo

Of the many genera belonging to the bamboo tribe, few are actually known to be a source of wax. The genera *Musa* (banana family) and *Sasa* appear to be the only ones that can be considered economic sources. They are gigantic herbs, the leaf stalks forming a trunk often more than a foot in diameter. The various species that are of interest include *M. textilis*, *M. paradisiaca sapientum*, *M. simiarum*, and *M. zebrina*.

The common banana, *M. paradisiaca* var. *Sapientum*, and *M. zebrina* van Houtte are recorded as having a coating of wax on the underside of the leaf, on fruit and petiole. Air-dried banana straw contains 1.76 per cent of wax and fat. *M. simiarum* Rumphius yields the rather well-known Pisang wax.

Pisang Wax. The leaves of the species *Musa simiarum* (*M. corniculata* Loureire, *M. acuminate* Coll.) of Pisang are about six feet long. The fruit is banana-like and is dried and ground in the unripe state into banana flour, known in Guiana as "Conquintay."

The natives in Java scrape off by knife the wax on the underside of the leaves. They can scrape about one half kilogram of wax from each 100 kilograms of leaves. These scrapings are then thrown into boiling water; the wax melts and floats to the top of the water from which it can be collected. The wax is marketed in cakes that are white, cream, or greenish in color, and transulcent. It is hard and can be easily pulverized.

Pisang wax, according to Greshoff and Sack[91], has a specific gravity (d^{15}) of 0.963–0.970, melts at 78–81°C, and has an acid value of 2–3 and a saponification number of 109. The wax is soluble in boiling turpentine, amyl alcohol, or carbon disulfide. It is sparingly soluble in solvents such as ethanol, acetone, and ether. The chemical composition of the wax has been given as an ester of a so-called *pisangcerylic acid* ($C_{24}H_{48}O_2$; m. 71°C), and *pisangcerylic alcohol* (m. 78°C). The former corresponds closely to the isomer of normal C_{24} acid, known as *carnaubic acid*, and the alcohol has the identical melting point of *isoceryl alcohol*. Hence Pisang wax most likely consists chiefly of *isoceryl carnaubate*, with a melting point of about 81°C.

Bamboo Leaf Wax. A wax derived from the leaves of *Sasa paniculata* Makino et Shibata, family Graminacæ, is brownish-yellow, hard, and

brittle, and somewhat resembles carnauba wax. This variety of bamboo grows abundantly in the mountainous districts of central Japan. Tuzimoto[285] refers to it as "nemagari-daké," and said he was able to extract about one per cent of crude wax from its leaves by means of petrolic ether. After a partial purification Tuzimoto determined the following constants for the wax: specific gravity (d^{25}) 0.961; melting point 79–80°C; acid value 14.5; saponification number 43.4; iodine number (Wijs) 7.8; and unsaponifiable matter approximately 65 per cent.

Bamboo leaf wax contains high-molecular-weight fatty acids (m. 81–82°C, neutralization value 121.8, iodine number 4.7), and unsaponifiable matter (m. 87–88°C, iodine number 12.7, acetyl value 58.9). Both *melissic acid* and *myricyl alcohol* were identified in the wax, which components apparently exist combined as the ester, *myricyl melissate*. Alcohols or esters corresponding to *montanic* and *cerotic acids* are possibly also present, but there is no appreciable amount of sterols.

(4) Waxes of Broad-Leaf Trees

The leaves of the palms, although belonging under the above classification, have been described separately (p. 155). The broad leaves of the oak, maple, beech, walnut, and innumerable other trees contain wax in minute proportions, as do the leaves of succulent plants, such as kohlrabi, spinach, corn, turnip, etc. Wax may be recovered by distilling off the moisture of mature leaf meal with xylene, collecting the xylene extraction residue, evaporating the solvent, and purifying the wax-resin mixture. Waxes are also recoverable from residues obtained in the long standing of essential oils steam-distilled from certain essential oil-bearing plant leaves.

The constituents of the broad-leaf waxes are mostly aliphatic alcohols, ketones, steroids, and hydrocarbons, all of which are largely in the uncombined form. Esters are present as derivatives of the fatty acids, usually of C_{14} to C_{28} range.

As an example of the chemical composition of leaf waxes, the leaf branch of the maidenhair tree (Chinese ginkgo tree), *Gingo biloba* L., was shown by Sosa[257] to contain *ceryl alcohol* ($C_{26}H_{53}OH$, m. 79.5°C). Branches of the male tree yielded a sterol of 137°C melting point. The branches contain as high as 4 per cent of raffinose. The leaf of the wild senna, or globedaisy, *Globularia alypum* L., a southern Europe shrub, yielded 0.75 per cent of waxy material, which Jacini[118] found to contain 20 per cent of a hydrocarbon, $C_{30}H_{62}$ (m. 65°C), and 15 per cent of *ceryl alcohol* ($b_{0.02}$ 175°C, m. 80.5°C). The ether extractive also contained glycerides and unsaponifiables not fully identified. The glycerides contained *palmitic*, *cerotic*, and *linoleic* acids, and a new type of *ricinoleic acid*.

Amyrins, lupeol, triterpene acids, and sapogenins of complex steroidal

ketonic structure are also encountered as chemical constituents of plant leaves. The leaf of *Theobroma cacao* L., family Sterculiaceæ, growing from Brazil to Mexico, contains a lipid wax that consists principally of β-amyrin palmitate, and which was isolated in 1892. The unsaturated free sterol content of the leaves of vegetables ranges from 0.6 to 1.6 mg per g, whereas the corresponding roots contain 0.25 to 0.5 mg, based upon the measurements made by the microchemical method of Wall and Kelly (see p. 597).

Ursolic acid (β-ursolic acid, m. 284–286°C), which is classified as a sapogenin, occurs in the leaf of the pituri shrub, *Duboisia hopwoodi* F. Muell., family *Solanaceæ*. In fact the leaf of the pituri contains 1 to 2 per cent of its dry weight of ursolic acid and appears to be one of the best sources of the acid. The acid is readily obtained as a crude by-product in the commercial alkaloidal (piturine and hyoscyamine) extraction of the leaf. For chemical structure of ursolic acid, see page 287.

Wax of Eucalyptus Species

Leaves of trees which yield essential oils contain a minute amount of wax which can be recovered from the oil residue accumulating on prolonged storage, for example, wax from the essential oil of eucalyptus. Of the 200 species of eucalyptus in Australia, about 25 yield valuable essential oils consisting principally of eucalyptol and pinene. One of the preferred economic species is the oil mallee eucalyptus *Eucalyptus oleosa* F. Muell., varieties of which yield 3 to 5 per cent of oil. Another is the Tasmanian bluegum, *E. globulus* Labill., also of the family order Myrtaceæ; the tree is indigenous to eastern Australia and Tasmania, and cultivated in southern Europe, California and the southern United States. The mature leaves are collected, dried, and steam-distilled to obtain several per cent of volatile oil.

The wax was first isolated from the oil of *E. acervula* Hooker, otherwise known as the "redgum" of Tasmania. Baker and Smith[17] gave the name *stearoptene* to the isolated paraffinic hydrocarbon. It melts at 55–56°C, and they regarded it as a mixture of C_nH_{2n+2} homologs of higher melting point, such as *heptacosane* and *nonacosane*. The wax has since been isolated from the oil of *E. paladusa*, and from the oil of *E. smithi* Baker. When purified the paraffin from the latter melted at 64°C, the melting point of *nonacosane*. Aliphatic paraffins are not uncommon constituents of essential oils.

Wax of *Bridelia* Leaf

The leaves of the indigenous drug, *Bridelia stipularis* Blume, when extracted with ether yield 10.5 per cent of wax. The wax is said to contain esters of *cerotic*, *palmitic*, and *stearic acids*, and of some liquid acids. *Bridelyl*

alcohol, $C_{22}H_{45}OH$ (m. 84°C), was separated from the unsaponified wax, and the coexistence of other higher alcohols was indicated, according to a bulletin of the Central Research Institute, University of Travancore, India.

Wax of *Cassia Fistula* Leaf

The leaves of the goldenshower senna, *Cassia fistula*, one of many species of the senna family, are reported by Modi and Khorana[191a], of the University of Bombay, to contain a wax. The pulp of the foliage was extracted with ethanol, and the residue of the extract treated before and after hydrolysis to obtain certain anthraquinone derivatives, a small amount of volatile oil, and waxy substances. The latter melted at 52–53°, 64–68°, and 114–116°C respectively. Accompanying the wax was an aromatic resinous substance which softened at 80°C and melted at 95–98°C.

Wax of Parasitic Plants

In the cohort *Santalales* there are three orders which are parasitic or mostly so, and that are wax-bearing. These orders are the Balanophoreæ, Santalaceæ, and Loranthaceæ. The latter is the mistletoe family of which there are many species; they are evergreen parasitic shrubs. The mistletoe, *Viscum album* L., is the source of "bird lime"; it contains some wax on its leaves but most of the wax is on the covering of the berries (see p. 279).

The leaf of the white sandalwood, *Santalum album* L., yields two unusual substances not generally found in plant waxes, namely *palmitone* and *d-10-hydroxypalmitone*. The wax from the leaves contains but little fatty acid. The unsaponifiable according to Chibnall and associates[51] comprises:

Primary Alcohols:	50 per cent
octacosanol (37½%)	
triacontanol (12½%)	
Palmitone:	44 per cent
d-10-Hydroxypalmitone:	6 per cent
(m. 96.5°C, $[\alpha]_D^{17.5} + 0.8°$)	

The plants of the family Balanophoreæ are tropical root-parasites and develop tuberous rhizomes and fleshy shoots which are yellow and without foliage leaves. Some of the species are rich in wax.

Balanophora Wax

The plants of the family Balanophoraceæ are indigenous to tropical or subtropical regions. They are root parasites. *Balanophora elongata* Foster, a parasite with a red and yellow flower, is found on Mt. Gedeh in Java. It grows on the roots of Ficus and other plants, and contains much wax and resin. *Langsdorffia hypogoea* Martius, of the same family, indigenous to tropical America, bears a flower with an edible torus. The plant is rich in

wax and in New Granada it is sold under the name of "siejas" and burned like a candle. The natives make a paste from the plant and coat the ends of wooden sticks with it, for use as torches.

The wax may be extracted by boiling the plant in water; it melts below 60°C, separates, and floats to the surface when it may be skimmed off and strained, or allowed to concrete as the liquor cools, and then be removed. It has a density of 0.995 at 15°C. It is soluble in ether, and sparingly soluble in ethanol. The wax will dissolve in cold sulfuric acid from which it may be reprecipitated by water. It is a resinous wax and contains glycerides. The wax of *Balanophora* spp. contains β-amyrin, (m. 195°C), combined with palmitic acid as balanophorin (m. 65°C?,) which natural ester was discovered as early as 1841 by Göppert. (The synthetic ester β-amyrin palmitate melts at 77°C.)

(5) Waxes of Narrow-Leaf Trees

The only really large and important division of existing plants of the Gymnosperms is the Coniferales. The leaves of conifers are usually characterised by their small size, e.g., the needle form represented by *Pinus*, *Cedrus*, *Larix*, etc., and the linear flat or angular forms, appressed to the branches, of *Thuja*, etc. All of the conifers bear cones.

Waxes of Conifers

Bougault and Bourdier[35] invesitgated the wax constituents of several conifers: the savin juniper, *Juniperus sabina* L., the common juniper, *J. communis* L., the Norway spruce, *Picea excelsa* L., the Scotch pine, *Pinus sylvestris* L., and the eastern arborvitæ, *Thuja occidentalis* L. These investigators found that these waxes were largely mixtures of compounds belonging to a class of natural products having the properties of acids, alcohols, and esters, but more or less in a combined form. They named the mixture of compounds "etholides," and provisionally assigned them the formula

$$RCH(OH)\,(CH_2)_n\,CO_2\,CHR'\,(CH_2)_n\,CO_2\,CHR''\,(CH_2)_n \cdots CO_2H$$

Chuit and Hausser[53] in 1929 set out to study polymethylene acid alcohols, to synthesize all of the hydroxy fatty acids consisting of 8 to 21 C atoms and study their properties. They prepared ω-hydroxycaprylic acid (m. 58°C), ω-hydroxynonylic acid (m. 51–51.5°C), and the simple etholide of the latter, which etholide (m. 60–61°C) contains 18 carbons:

$$CH_2\,(OH)\,(CH_2)_7\,CO_2\,CH_2\,(CH_2)_7\,CO_2\,H.$$

When the latter is heated to 200°C for one hour it combines with itself to form a double etholide (m. 71–72°C).

$$HO_2C\,(CH_2)_7\,CH_2O_2C\,(CH_2)_7\,CH_2O_2C\,(CH_2)_7\,CH_2O_2C\,(CH_2)_7\,CH_2OH$$

These investigators also prepared the simple etholide (m. 56–56.8°C) of 20 carbons. They synthesized *juniperic acid* and found it to be identical with the natural product derived from wax obtained from pine needles of the fir.

The dried pine needles of the silver fir *Abies alba* L. (*A. picea* Lindley) contain 0.17 per cent of *juniperic acid* (16-hydroxypalmitic acid, m. 95°C), and according to Chuit and Hausser[53] this acid on heating to 125°C may be converted to the etholide $C_{64}H_{122}O_9$ (m. 87.5–88.0°C). *Thuju occidentalis* also contains juniperic acid.

Bougault and Bourdier[35] isolated from the wax of the savin juniper (*J. sabina*) *juniperic acid* and *sabinic acid* ($C_{12}H_{24}O_3$, m. 84°C), later identified as *12-hydroxylauric acid*. The acetyl derivative of juniperic acid melts at 63°C, that of sabinic acid at 43°C.

The waxlike substances are extracted from the conifers by means of boiling alcohol (80%), and purified by recrystallization from hot ethanol (95%) after washing with ether to remove green coloring matter. The constants from the crude wax from *J. sabina* are: melting point 72–73°C, acid value 40, saponification number 241, acetylized product with acid value 40, saponification number 271. The purified wax melts at 80°C. The wax of *J. sabina* contains *juniperic*, *sabinic*, and *thapsic acids*. An allied species, the Sierra juniper, *J. occidentalis* Hooker, contains both α- and β-sitosterol.

Fujita and Yoshikawa[53a] have isolated a compound in the wax of *Juniperus rigida*, which upon saponification gives *ω-hydroxytetracosanoic acid* (24-hydroxylignoceric acid). The latter polymerized into a gummy substance and "etholide" of Bougault and Bourdier, a 7 molecular polymer. The compound has a molecular weight of approximately 2600. These investigators report that the wax was found to contain C_8, C_{10}, C_{12}, C_{16}, and C_{22} fatty acids in combination with *ceryl* and *myricyl alcohols*.

The crude lipid wax from the Norway spruce, *Picea excelsa* (L.) Lyons (*Abies excelsa* Poiret), has the constants: melting point 75–78°C, acid value 30, saponification number 227, acetylized product with acid value 28.5, saponification number 254. It contains etholides of hydroxy acids, particularly *juniperic acid*. A crude lipid wax obtained by extracting the young growing tops of the slashpine, *Pinus caribaea* Morlet, with petrolic ether is reported to contain paraffins of low molecular weight; *melissic acid*; *melissyl alcohol*; *nonacosan-10-ol*; *α-sitosterol* and *α-sitosterolin*; *palmitic*, *juniperic*, and *behenic* acids; oily acids (probably *oleic* and *linoleic*); and *abietic acid*.

Wax of the chermes of the Eastern whitepine, *Pinus strobus* L., is believed to be an ester of *17-keto-hexatriacontanol* (m. 102°C), and *11-keto-triacontanoic acid* (m. 103.4°C). A similar ester of homologs is found in cochineal wax. The needles of the Japanese black pine, *Pinus thunbergi* Parlatore,

contain a tasteless and odorless wax having the following constants: specific gravity (d^{17}) 0.9201; melting point 78–80°C; acid value 29.8; saponification number 218.9, ester value 189.1; saponification number after acetylation 219.2; iodine number 7.5. The Japanese call the wax "matsubaro." The chemical composition of the wax comprises esters of *lauric, palmitic, stearic,* and *hydroxypalmitic acids,* possibly combined with ketonic alcohols, or in the form of etholides. As Sakuri[238a] states it, "the OH group of the hydroxy acid is not free but is bound with other fatty acids."

Wax from the Eastern arborvitae, *Thuja occidentalis* L., has the following constants: melting point 76–84°C; acid value 33; saponification number 221; acetylized product with acid value 33; saponification number 254[35]. The wax contains etholides of *juniperic* and *sabinic acids,* alcohols in the range of C_{26}–C_{34}, and carotenoids.

Oriental Longleaf Plant Foliage Waxes

Kariyone and his co-workers (Univ. Kyoto)[120] have described several native longleaf foliage waxes and given a knowledge of their chemical composition.

Species of Plant	Source of Wax	Yield (%)	Melting Point
Chamaecyparis obtusa	dried leaves	1.8	67–72.5°C
Biota orientalis	dried leaves	0.5	78–79°C
Chamaecyparis pisifera	withered leaves	1.2	71–72°C

The dried leaves of the hinoki false cyprus, *C. obtusa,* had the following constants: acid value 49.2, ester value 171.8 (after acetylation 214.8), iodine number 18.6. Saponification yielded 83 per cent acids and 9 per cent unsaponifiable substance. The unsaponifiable consists of *myricyl alcohol, 1-12-dodecanediol* (m. 80–81°C), and *d-nonacosane-10-ol.* The wax contains neutral *estolides* (a long-chain ester of a hydroxy acid with itself) of 3–5 mols of *juniperic* (16-hydroxypalmitic) and *sabinic* (12-hydroxylauric) acids.

The white wax obtained from *T. orientalis,* commonly known as Chinese arborvitae, had the following constants: acid value 17.8, saponification number 225.7, and ester value 207.9. Saponification of the wax gave 81 per cent acids (mostly *juniperic* with a small amount of *sabinic* in estolides form, and 7 per cent of unsaponifiable of which *pentatriacontane* and 1,16-hexadecanediol (m. 87–88°C) were isolated.

Sawara leaf wax from the withered foliage of the sawara false cyprus, *C. pisifera,* is a white wax which had an acid value 34.2, saponification number 165.2, ester value 131, and iodine number 13. Saponification of the wax yielded 73 per cent acids (mostly *juniperic* and *sabinic* in estlides form) and 21 per cent unsaponifiable (mostly *d-nonacosan-10-ol*), which is also contained in *Juniperus chinensis* and *C. obtusa.*

WAXES FROM GLANDS AND HAIRS OF FRUIT CAPSULES

There are certain species of fruit which bear capsules that have glands and hairs containing wax constituents. For example, *kamala*, an article of commerce, consists of glands and hairs of the capsules of the kamalatree, *Mallotus philippinensis* Mueller, Arg., family order Euphorbiaceæ. Kamala has long been known as an orange dyestuff, and for medical use. *Wurrus*, a variety of the same plant, but growing in India and Arabia, has been used as a substitute for kamala. Both kamala and wurrus (waras) have wax as one of their components.

The fruit hairs of the ceiba kapok, *Ceiba pentandra* Gaertner (*Eriodendron anfractuosum* De Candolle), family order Bombaceæ, have a wax constituent. The plant is indigenous to tropical America, but is mostly grown in Java, and to a lesser extent in South Africa, the Philippines and the East Indies. It is of value for its lint and to some extent for the oil which is produced from its seed. The hairs or lint are attached to the inner walls of the pod and not to the seed. The wax which obviously is of academic rather than economic interest, may be prepared by solvent extraction of the lint, of which it constitutes about 5 per cent.

Kamala has as its components a crystalline compound *rottlerin*, $C_{33}H_{30}O_9$, a lipid wax, and a resin $C_{12}H_{12}O_3$ (m. below 100°C). The wax itself is a crystalline material which melts at 82°C[274]. Wurrus is a powder which resembles kamala and yields flemingen, $C_{12}H_{12}O_3$ (m. 171–172°C), homoflemingin (m. 165–166°C), resins of lower melting points, and a wax.

Wax of Java Kapok Lint

Java kapok (*C. pentandra*) lint yields a wax which is semisolid and melts at 24°C; the low melting point is due to the *glycerides* of unsaturated acids, such as *oleic*, *linoleic*, and *linolenic*. Matthes and Streicher[134] of the University of Jena in 1941 reported on the analytical constants of the wax of Java kapok lint as follows: melting point 24°C, refractive index (n_D^{40}) 1.4618, acid value 59.8, ester value 110.3, saponification number 170.1, iodine number 69.4, R-M number 2.02, Polenske value 0.97, unsaponifiable 28 per cent. It is believed to contain *myricyl alcohol* and *phytosterol* as components. The fatty acids consist of *palmitic acid* in part combined with the alcohol components; and unsaturated acids, previously mentioned. *Acon wax* prepared from acon fiber, similar to Java kapok, is of similar chemical composition, and is reported to also contain a hydrocarbon. Acon wax melts at 30.5°C.

WAXES FROM ROOTS AND RHIZOMES

Very small amounts of wax are obtainable from the roots of herbs. These lipid waxes are often referred to as root fats. Lipid wax-containing species

are *Alkanna tinctoria, Taraxacum officinale, Gentiana lutea, Exogonium purga, Ipomea orizabensis.* The wax is generally difficult to separate from the resinous constituents, and has no economic value.

The true root fats are comprised of *palmitin, stearin, arachidin, olein* and *linolein*, and therefore do not fall in the category of waxes. Tropical sedges, poke root, senega root, etc. have oleic, palmitic, and linoleic as major component acids, and stearic and arachidic as minor components. With the root fats are occasionally associated waxy and resinous principles.

The tuberous root of the herb jalap, *Exogonium purga* Bentham (*Ipomoea purga* Hayne), of the family Convolvulaceæ, contains 6 or 7 per cent resin, from which may be isolated waxy lipid constituents such as a *phytosterol* and *cetyl alcohol* (m. 50–51°C) in the saponifiable matter. The phytosterol is apparently β-sitosterol, since it has the formula $C_{27}H_{45}(OH)\cdot H_2O$ (m. 134–135°C, $[\alpha]_D$ −34°C). The root of Mexican scammony, also known as male jalap or orizaba root, *Ipomea orizabensis* Pell., contains a lipid wax from which *jalapinolic* (11-hydroxyhexadecanoic) acid has been isolated. The wax also contains *hentriacontane*; a *phytosterol*, $C_{27}H_{46}O$; *cetyl alcohol*; and a mixture of *palmitic, oleic, linolenic,* and *linoleic acids.*

Wax from Alkanet Root

A wax is obtainable, according to Betrabet and Chakravarti[27], from the root of the dyer's alkanet, *Alkanna tinctoria* (L.) Tausch, family Boraginaceæ. The powdered root is extracted with petroleum ether; the extract is evaporated and then treated with acetone, leaving behind a reddish white wax. By refluxing with methyl ethyl ketone and boneblack for four hours, and then concentrating the filtrate, white flakes of wax are obtained which when crystallized from ethyl acetate melt at 78°C. The yield is 0.18–0.2 per cent from the powdered root. The analytical constants for the wax are as follows: density (d^{30}) 0.9676, refractive index (n_D^{80}) 1.438, saponification number 69.2, acid value 12.9, unsaponifiable matter 58.6 per cent, iodine number 12.2, molecular weight of mixed acids 380.

After saponification with alcoholic NaOH, the soap was extracted with ether; the residue, acidified with HCl, gave two acids: one (m. 68°C) of undetermined nature; the other (m. 76°C) *cerotic acid.* The ether extract of the soap was evaporated and the residue, recrystallized from ethanol, melted at 68°C and proved to be *carnaubyl alcohol.* On oxidation with chrome-acetic acid it gave a white solid (m. 72°C) from ether, which is *carnaubic acid.* Hence the wax is chiefly *carnaubyl cerotate.* The wax is obtainable as a by-product when extracting alkanet root for its coloring principles.

Wax of Dandelion Root

The common dandelion, *Taraxacum vulgare* Shrank (*T. officinale* Wiggers), family Cichoriaceæ, contains a lipid wax in its root. The wax is recorded by Inoue[115a] as having the following constants: melting point 152°C, acid value 17.8, saponification number 114.9, iodine number (Wijs) 25.8, optical rotation $[\alpha]_D^5$ +47.2.° Power and Browning[212] in 1913 isolated from the water-insoluble resin obtained from an alcoholic extract of the roots of dried English plants, two monohydric cyclic alcohols (pseudosterols) of the type, $C_nH_{2n-11}OH$. One alcohol they named *homotaraxasterol*. It crystallized in needles [m. 163–164°C, $[\alpha]_D$ +25.3]. The other they named *taraxasterol*, which also crystallized in needles [m. 221–222°C, $[\alpha]_D$ 96.3]. These investigators postulated that these alcohols fell in line with the C_{27} and C_{30} pseudosterols with one oxygen atom which were isolated by Moore[194] from the rhizome of the spreading dogbane, *Apocynum androsæmifolium* L., family Apocynaceæ. (These pseudosterols are *homoandrosterol*, $C_{27}H_{45}OH$ (m. 192°C), and *androsterol* $C_{30}H_{49}OH$ (m. 209–210°C, $[\alpha]_D$ +30.)

Recent investigations indicate also that there are two phytosterols in dandelion root, namely *β-sitosterol*, $C_{27}H_{45}OH$, and *stigmasterol*, $C_{29}H_{47}OH$. Taraxasterol preferably called *taraxastol*), which has the formula $C_{30}H_{49}OH$, is believed to belong to the amyrin-lupeol class of triterpenoid alcohols (see p. 31). A tetrahydric alcohol, *cluytianol*, has also been isolated. The acid constituents, largely combined as esters, are *palmitic*, *cerotic*, *melissic*, and a small amount of unsaturated acids.

Wax of Gentian Root

Yellow gentian, *Gentiana lutea* L., family Gentianaceæ, growing in Sardinia, has been found by Binaghi and Falqui[29] to have a wax principle in its root. The fresh root was pulverized and digested with five times its weight of 95 per cent ethanol; the extract was then evaporated *in vacuo*, and the residue extracted with cold petroleum ether and evaporated. The product constituted 3.4 per cent of the weight of the root, and was of yellow-red and oily nature. When this oily material was saponified with alcoholic potassium hydroxide, extracted with ether after removal of the ethanol, and then diluted with water, a wax appeared. This wax crystallizes from ethanol in fine needles, and has a melting point of 142–143°C. It is insoluble in water, but soluble in chloroform, benzene, petroleum ether, vegetable oils and glycerol. The waxy principle is referred to as *gentiosterine*, and has a specific rotatory power of $[\alpha]_D^{20} = -29.4$°C (in chloroform).

WAXES FROM BARKS OF TREES AND SHRUBS

Waxes ranging in quantity from a minute to large amount are found in the barks of trees. For example, the amount of wax recoverable from the

bark of *Betula lenta*, *Ligustrum vulgare*, *Fagus sylvatica*, or most of the trees is varying small, whereas the barks of *Pseudotsuga taxifolia* and *Pinus ponderosa* contain several per cent of wax. Shrubs which have wax-bearing barks include *Nerium odorum*, *Fouquieria splendens*, *Moquinia hypolenca*, *Calotropis gigantea*, and *Alstonia scholaris*.

There are but a few barks that can be utilized to produce wax in commercial quantities. Outstanding exceptions are the barks of the douglasfir, and ponderosapine, which are not only rich in wax, but afford other by-products of value. These barks are recoverable from the sawmill wastes of the timber companies operating in the Northwest of the United States.

The waxy matter of a bark ordinarily consists of (a) fatty acid esters of one or more straight-chain alcohols; (b) cyclic alcohols free and/or combined; (c) occasionally a higher hydrocarbon with an odd number of carbons, some of which ostensibly have a methyl (CH_3) side chain, or a carbonyl (CO) linkage; (d) resin acids. The normal fatty acids naturally occur with an even number of carbons, and in free as well as combined state. Alcohols with an odd number of carbons have frequently been reported as bark wax constituents; most of these are cyclic in structure. Amyrenols (amyrins) or lupeol have a five-membered ring structure (picene) and are of the formula $C_{30}H_{50}O$, although Dieterle[68] assigned the formula $C_{31}H_{50}O$ to lupeol.

The presence of α-amyrenol (m. 186°C, $[\alpha]_D$ 75.8°C) and/or β-amyrenol (m. 197.2°C, $[\alpha]_D$ 88.2°C) in the waxy matter of bark is not uncommon. The wax of the sweet birch, *Betula lenta* L., contains the principle, *betulin* (m. 251°C), to the extent of about 10 per cent. Betulin is grouped with the amyrins (see p. 31), and is believed to be $C_{30}H_{48}(OH)_2$, although $C_{30}H_{50}(OH)_2$ is not impossible. The acetone-soluble portion of the unsaponifiable matter isolated from the petrolic ether extract of the bark of the red mulberry tree, *Morus rubra* L., yields colorless needles (m. 180–195°C), which have been identified as α-amyrin. The phytosterol present in the waxy material of tree bark is usually *sitosterol*, $C_{27}H_{45}(OH)$.

Ponderosa Bark Wax

The air-dried bark of the ponderosa pine (Western yellow pine), *Pinus ponderosa* Laws., when extracted with hexane yields 3.4 per cent of a yellow wax (m. 56–58°C); and on further extraction with benzene yields 1.3 per cent of a brown wax (m. 58–60°C). According to Kurth and Hubbard[145a], in the western states there is an annual lumber production of 3 billion board feet of ponderosa pine, and currently the sawmills use the bark for fuel, or send it to the refuse burners. These investigators room-dried bark taken from saw logs at Sisters, Oregon, to a moisture content of less than 10 per cent, and then ground the bark to pass a 25-mesh sieve before extract-

ing it with hexane (b_{60-70}°C) and subsequently with benzene. The yellow wax was dissolved in ether and separated into a "free acid fraction" and a "neutral fraction" by extraction with 5 per cent potassium carbonate solution.

The free acid fraction was found to contain *behenic* and *lignoceric acids* and also *resin acids* and unsaturated fatty acids. The resin acids have a melting point of 82–83°C, a neutral equivalent of 346.5, and a specific rotation $[\alpha]_D^{25}$ in ethanol of +39.5°C. The unsaturated fatty acids have a neutral equivalent of 194 and an iodine number (Hanus) of 93.4, and yielded dihydroxystearic acid (m. 129–130°C) when oxidized with cold $KMnO_4$, indicating the acids to be *oleic acid*, and possible small amounts of more highly unsaturated acids.

The "neutral fraction" was steam-distilled to recover any volatile oil present. There was obtained 0.2 per cent of an oil having characteristics of a mixture of α- and β-pinene, dipentene, borneol, and borneol acetate. After steam distillation the neutral fraction had a melting point of 59–60°C, and a saponification number of 84.0. It was separated into saponifiable acids and unsaponifiable matter by saponification with alcoholic potassium hydroxide. The acids were crystallized from acetone to a constant melting point of 69 to 70°C and a neutral equivalent of 330, which indicated a mixture of *arachidic* and *behenic acids*. The unsaponified fraction was recrystallized from ethanol. It yielded a trace of a sterol (m. 137–138°C). After removal of the ethanol it was recrystallized from acetone. The white precipitate of fatty alcohols was oxidized to the corresponding acids by

TABLE 54. CHEMICAL COMPOSITION OF YELLOW WAX OF PONDEROSA BARK (by Kurth and Hubbard)[145a]

Free Acids:	42.1 per cent
Saturated fatty acids, 21.2%	
Unsaturated acids (oleic acid present), 1.4%	
Resin acids, 19.5%	
Combined Acids:	29.8 per cent
Saturated fatty acids, 29.9%	
Unsaponifiables:	28.1 per cent
Fatty alcohols, 27.2%	
Phytosterol, 0.7%	
Volatile oil, 0.2%	

TABLE 54a. CONSTITUENTS OF BROWN WAX OF PONDEROSA BARK

	Per Cent
Hexane-soluble fatty acids	34.0
Ethanol-soluble fatty alcohols	23.5
Ethanol-insoluble alcohols	3.5
"Phlobaphene"	39.0

fusion with KOH; the acids obtained correspond to the equivalent of a mixture of *behenyl* and *lignoceryl alcohols*.

Extractives other than wax are obtainable by subsequent extraction of the wax-free residues with ethyl ether to obtain 0.83 per cent of a yellow coloring matter (pentahydroxyflavone); with 95 per cent ethanol to obtain 8.3 per cent tannin and phlobaphene; and with hot water to obtain 12.13 per cent of tannin, carbohydrate, etc. The phlobaphene-like material is believed to be phlobaphene-fatty acid complex which lends its color to the brown wax. Phlobaphene is 3,3′,4′,5,8-pentahydroxyflavone. The tannin is an "acid-producing tannin" comparable to chestnut tannin extract.

Wax of Beech Bark

The bark of the European beech, *Fagus sylvatica* L., family order Fagaceae, contains a fraction of one per cent of lipid wax. The wax melts at 64°C. Although the wax apparently has no economic value, it has been the subject of study by several investigators. Clotofski and co-workers[55] estimated that the waxy material amounted to 2½ per cent of the methanol extractive of the ground bark. In their method they triturated the bark with hot methanol; the extract, after filtering and cooling, leaves an insoluble portion which is composed of a hydrocarbon (m. 63–65°C), probably *nonacosane*, and a wax which upon saponification and distillation *in vacuo* yields an alcohol, $C_{20}H_{42}O$ (m. 73°C), and an acid, $C_{20}H_{40}O_2$, purified through the lead salt. If water is added to the cold-soluble portion of the extract an insoluble portion arises, which when treated with sodium carbonate leaves waxy material: *arachic alcohol* (m. 72.5–73°C), Hess' *phytosterol* (m. 132°C), and a compound (m. 225–227°C) which reacts as a sterol.

By extracting the bark with low-boiling petrolic ether, Clotofski and Herr[56] found that the precipitate obtained in concentrating the extract consists of *ceryl alcohol* (m. 77–80°C), and a substance $C_{20}H_{48}O_2$ (m. 232°C) which has not been fully identified. The filtrate evaporated *in vacuo* consisted of a greenish pitchy residue, amounting to less than 0.2 per cent of the weight of the bark. The residue when saponified yielded *arachidic acid*, $C_{20}H_{40}O_2$ (m. 75°C), and a sterol which ostensibly is combined with the latter as an ester. The sterol possesses a double bond, melts at 134°C, and is levo-rotatory, $[\alpha]_D$ −31.5°. Its acetate, $C_{28}H_{42}O_2$, melts at 121–122°C, and is levo-rotatory, $[\alpha]_D$ −32.4°. Zellner[329] found a ceryl ester of an acid $C_{20}H_{40}O_2$ (m. 80°C), which had a neutralization value 179.4. He also in 1926 had determined that phytosterol is a constituent of beech bark. In determining the type of phytosterol, Clotofski *et al.*[55] noted that the acid products of saponification yield an acid, $C_{24}H_{48}O_2$ (m. 70–71°C, carnaubic ?), and resin acids.

Waxes of Barks of other European Species

From the cork bark of the European elder tree, *Sambucus nigra* L., family order Caprifoliaceæ, Scurti and Tommasi[243a] in 1913 isolated a waxy alcohol (m. 287–280°C), $C_{31}H_{56}O_2$, closely resembling *oleanol*. [The oleanol of Power and Tutin derived from olive leaves had been assigned the formula $C_{31}H_{48}(OH)_2 \cdot H_2O$ (m. 303–304°C, $[\alpha]_D$ 78.3°), and was believed to be a hydroxyphytosterol with a perhydrophenol group attached]. They also identified the acid constituent of the cork as α-hydroxybehenic acid. In 1926 Zellner[329] isolated from *S. nigra* both an alcohol, $C_{23}H_{40}O_2$ (m. 216°C), and an alcohol, $C_{27}H_{48}O$ (m. 179°C). Transformation of the C_{31} alcohol into fatty acids is said to take place in the leaves.

Zellner[329] found that the bark of the European privet tree, *Ligustrum vulgare* L., yielded waxy matter which comprised *ceryl palmitate*; *ceryl alcohol*; a *palmitic ester* of an alcohol $C_{25}H_{42}O$, or $C_{25}H_{44}O$ (m. 215°C); *phytosterol*; possibly *esters* of *behenic* and *arachidic acids*; and *platanolic acid*. From the bark of the tree, European green alder, *Alnus viridis* L., he obtained *ceryl alcohol*; an alcohol $C_{33}H_{60}O_2$ called *alniviridol* (m. 194°C): and an alcohol $C_{24}H_{42}O_2$ (m. 250°C).

Zellner[329] reported that the bark of the bloodtwig dogwood, *Cornus sanguinea* L., yielded a substance similar to *alnulin*, $C_{30}H_{52}O$ (m. 251°C, Ac. deriv. m. 237°C); a phytosterol $C_{25}H_{44}O \cdot H_2O$ and *platanolic acid*, $C_{24}H_{40}O_3$. From the bark of the bigleaf linden, *Tilia platyphyllos*, he obtained *ceryl alcohol*, *sativic acid*, $C_{18}H_{36}O_6$, and an alcohol $C_{22}H_{38}O_3$ (m. 285°C). The bark of the European hornbeam, *Carpinus betulus* L., yielded *ceryl alcohol*; an alcohol $C_{18}H_{24}O_2$ (m. 249°C, Ac. deriv. 217°C); *dihydroxystearic acid*; and *sativic acid*.

Birch Bark Wax

The outer bark of the sweet birch, *Betula lenta* L., of the European white birch, *B. verrucosa*, and probably allied species, contains a wax. This wax is not unlike the wax of the cork bark, *Quercus suber* L. In 1926 the Vesterbergs[304], noting that Tunmann had found 12–14 per cent of steroids in the outer bark, the principal one of which was called *betulin* and appeared to be analogous with *amyrins*, $C_{30}H_{49}OH$, determined to work on its constitution.

From an alcoholic extract of the bark by means of separating the impurities with alcoholic lead acetate they obtained about 10 per cent of pure betulin (m. 251°C). They found the formula $C_{30}H_{48}(OH)_2$ well founded, though $C_{30}H_{50}(OH)_2$ is not impossible. They also found that betulin has one mol of alcohol of crystallization, which can be driven out at 125–130°C. Several derivatives were prepared, including the monoacetate (m. 260.3°C).

Jensen and co-workers[119b] found that the outer bark of the European white birch, *B. verrucosa*, (*B. pendula*), contained 38.7 per cent of *suberin*,

which is considered to be a "polyestolide." From the polyestolide they liberated the OH fatty acids and obtained: (a) $C_{22}H_{42}O_4$ (m. 124.3°C) which had two COOH groups, no MeO or OH groups, and no double bonds. [It is apparently *eicosane dicarboxylic acid* (*docosanedioic acid*)]. (b) $C_{22}H_{44}O_3$ (m. 99.3–99.6°C) which had one COOH group and one OH group. It corresponds to *22-hydroxybehenic acid* (phellonic acid). (c) A new acid $C_{18}H_{34}O_4$ (m. 81.8–82°C) which has one COOH, no MeO, and one OH group, and one double bond. The acid has not as yet been fully identified.

Cork Wax

The cork oak tree, *Quercus suber* L., is native in the vicinity of the Mediterranean Sea where it is a prominent feature of the vegetation in about 5,000,000 acres of natural forest situated in Portugal, Spain, Italy, North Africa, Greece and the Mediterranean Islands. The outer bark of cork oak is known commercially as "corkwood"; it has been harvested for many years without injury to the trees which can be stripped at about ten-year intervals until well over 100 years.

Corkwood contains 5 to 10 per cent of a waxy material sometimes referred to as cork wax. The wax can be extracted from the corkwood, if dry and well ground, by means of an organic solvent (e.g., ethyl acetate), but is soft and impure. According to Šorm and Bažant[256a] (Tech. Univ. Prague), 20 per cent of neutral components may be extracted from the corkwood by means of a cold mixture of ethanol and benzene. Very little of the extractive matter has real waxy characteristics. Attempts made to purify the extractive matter generally lead to obtaining crystalline components which have no waxy properties.

Dupont and Guillemonat[71] claim they can produce a commercial cork wax by first treating a mass of cork with an aqueous solution of sodium hydroxide, then adding mineral acid in an amount corresponding to the alkali used; the insoluble products are separated from the acid solution by a solvent (preferably a mixture of acetone and methanol) and the solvent distilled off to leave the wax. The wax is of a brownish color and has a melting point of 70°C, and an acid index of 224–254 (g KOH fixed per kg of product). If this wax is extracted with trichloroethylene or carbon tetrachloride a colorless product (m. 50–70°C) with an acidity index of 254–311 is obtained; it has a resinous appearance and can be polymerized.

In the production of long stoppers in Portugal the offal or waste product has been extracted on a commercial scale to produce a wax of considerable hardness, and which is of use in the manufacture of shoe pastes, etc. This wax is prepared by Aguiar & Mello, L. da Praco do Municipio, 13 Loja, Lisbon, Portugal. Information concerning its mode of preparation is not available. The wax is brownish in color. In its raw state it contains 0.82

per cent moisture, and a fraction of one per cent of cork particles, resin, and mineral matter. It has a melting point (drop) of 85.7°C (186.3F); ball and ring 86.2°C (174.2°F); Fisher-Johns melting point 79°C minimum, 82.5°C maximum; softening point (in water) 79°C. The cork wax is very hard, and gives a penetration reading (100 g/5 sec/25°C) of 2.9.

Composition of Waxy Extractive from Cork. The chemical composition of the extractive matter obtained from cork has evoked considerable interest because of the peculiar nature of some of the components. Fierz-David and Ulrich[78b] reported that an exhaustive extraction of ground bark from oak trees (*Q. suber*) with alcohol and/or benzene covering a period of several weeks dissolves about 20 per cent of substances which proved to be a mixture of waxes and terpenes. The residue on saponification with 3 per cent sodium hydroxide yielded a mixture of fatty acids comprising about 50 per cent of the ground bark. The undissolved residue consisted of lignin and cellulose. The approximate analysis of the bark is water 7, alcohol-soluble materials 20, saponifiable 50, cellulose 11, and lignin 20 per cent.

In 1916 Scurti and Tommasi[248] at Turin isolated the component *cerin* (m. 247–251°C) from corkwood. Cerin crystallizes in white needle-like laths, and according to Drake and Jacobsen[69] it is a hydroxy ketone of cyclic structure with the empirical formula $C_{30}H_{50}O_2$, and is optically active, $[\alpha]_{5461}^{27}$ −44.5°. The cerin in its crude state was extracted from cork with ethyl acetate and the yield was 5–10 per cent. From the mother liquor these investigators recovered another ketone, *friedelin*, which crystallizes out in white, broad laths (m. 255–261°C) and has the composition $C_{30}H_{50}O$, and is also optically active, $[\alpha]_{5461}^{20}$ −29.4°. Cerin and friedelin are polynuclear compounds (four rings and one double bond in friedelin), and are quite stable. These triterpenoids can be seen in the cork cells under high magnification.

Šorm and Bažant[256a] by chromatographic separation of the ethanol and benzene extractive produced *cerin*, *friedelin*, and $C_{24}H_{50}O$, a cyclic alcohol of uncertain purity, but which yields a $C_{24}H_{50}O_2$ acid (m. 75°C) on oxidation, also paraffinic alcohols in small quantity. In succeeding fractions they isolated a tricyclic saturated alcohol, $C_{20}H_{36}O$; a triterpene dialcohol, $C_{30}H_{52}O_2$; a triterpene hydroxy ketone, $C_{30}H_{50}O_3$; and a diterpene fraction (m. wt. 347, m. 290–292°C) not fully identified, and which may be $C_{20}H_{34}O$, or $C_{25}H_{42}O_2$. Friedelin which is a major component of the noncellulosic constituents of cork has no wax like properties. Drake and Jacobsen[69] reported the presence of a small amount of *sterol*, $C_{28}H_{50}O_2$, which melts at 65–70°C, and clears at 145°C.

According to Zetsche and Lüscher[330] the hydroxyketone and ketone constitute 18–19 per cent of the wax crude. The wax contains 10 per cent of steroids, possibly including a pentacyclic dihydric alcohol, $C_{30}H_{48}(OH)_2$,

belonging to the lupeol-betulin group, and associated with other barks as well. These investigators reported that cork contains 2 per cent of an alcohol, $C_{24}H_{42}O_2$, which is a dihydroxy steroid of the $C_nH_{2n-8}(OH)_2$ type. They also reported that they had found *phytosterol* in the steroids of the wax but only to the extent of 0.6 per cent.

The acids of cork were first observed by Höhnel in 1877; one called *phellonic acid* was isolated by Kügler[142] in 1884. This was assigned the formula $C_{22}H_{42}O_3$ (m. 96°C), but in 1941 Drake and his collaborators[65a] showed the acid component of cork to be *22-hydroxytetracosanoic acid* ($C_{24}H_{48}O_3$, m. 93–93.5°C) and this was confirmed by Erlenmyer and Müller at the University of Basil, Switzerland in 1945. Phellonic acid when fused with KOH and the acid liberated by HCl and purified by crystallization yields *1,20-eicosanedioic acid*, $C_{20}H_{40}O_4$, which melts at 123.5–124.5°C (the synthetic acid melts at 121–123°C). Its methyl ester melts at 71–72°C (synthetic Me ester melts at 68–69°C). The C_{22} dicarboxylic produced from phellonic acid of cork is now known as *phellogenic acid*. Ribas and Curbera[230a] of the University Santiago, Santiago de Compostela, Spain, prefer the structure, *φ-hydroxybehenic acid* rather than the C_{24} structure of Drake *et al.* The acid is soluble in methanol only to the extent of 0.15 per cent at 20°C. The C_{22} structure of phellonic acid had also been advanced by Zetsche and Sonderegger in 1931, although the OH group was placed in the "alpha" instead of "phi" position. They reported that pure phellonic acid crystallized from chloroform melts at 96°C, and its acetyl derivative at 79°C.

Zetsche and Sondregger[330] in 1931 boiled cork with a sodium sulfite (Na_2SO_3) solution, and isolated the so-called waxy alcohols (in reality ketones) *friedelin* and *cerin* from the sulfite water extraction by means of carbon disulfide. They saponified the residue by treatment with alcohol and boiling alcohol and liberated the acids by HCl. These investigators isolated *phloionic acid*, a crystalline solid; *suberinic acid*, a semiliquid; and *suberotic acid*, a semisolid. Scurti and Tommasi[248] in 1910 reported that *suberinic acid* is ricinoleic acid ($C_{18}H_{34}O_3$), and *phloionic acid* is a tricarboxylic aliphatic acid [$C_{22}H_{42}(COOH)_3$, m. 121°C]. Cooke[59] in 1944 listed the fatty acids in cork as *phellonic* ($C_{22}H_{44}O_3$, m. 96°C); *1,20-eicosanedioic acid* ($C_{22}H_{42}O_4$, m. 123.5–124.5°C); *phloiconolic* ($C_{18}H_{36}O_3$, m. 104°C); and *phloionic* ($C_{18}H_{34}O_6$, m. 124°C). Phloionic acid is now believed to be *9,10-dihydroxyoctadecanedioic acid* ($C_{18}H_{34}O_6$, m. 121°C).

Curcas Wax

Curcas wax is mentioned by Lewkowitsch as occuring on the bark of the barbadosnut, *Jatropha curcas* L., of the order Euphorbiaceæ. The seeds of this plant by hot-pressing yield curcas oil, an oil of some economic impor-

tance to Cape Verde Islands and other Portuguese colonies. In the West Indies and in South America the tree is known as the "purging-nut tree," and the seeds as "piñon." The wax consists chiefly of *melissyl alcohol* and *melissyl melissate*. The oil is used in Portugal for soap making, as an illuminant, and as a lubricating oil, for which purpose it is not particularly suited. In medicine the oil is used as a purgative. The wax has not been commercially exploited.

Wax of White Spruce Bark

The bark of white spruce, *Picea canadensis* Mill. (*Picea alba* Link.), family Pinaceæ, contains a wax. When white spruce bark is extracted with methanol and the extract is concentreated to 70–75 per cent solids and then diluted with 1.6 parts of water, a waxy material is precipitated. If this precipitate is dried and extracted with ether, the extractive contains resin acids and a mixture of fatty acids and esters. *Lignoceric acid*, *behenic acid*, and *lignoceryl alcohol* were separated by Bishop and co-workers[29a] from a wax softening at about 56°C. *Oleic*, *linoleic*, and *linolenic acids* were also identified. The nonsaponifiable portion contained 5 per cent of crystalline plant *sterols* and a dihydroxyditerpene, $C_{20}H_{34}O$.

Douglasfir Wax

The bark of the common douglasfir, *Pseudotsuga taxifolia* Lamb., of the family Pinaceæ, indigenous to a region from Puget Sound to California, contains a large amount of wax, obtainable in good yield. The wax, accompanied by resinous matter, is interspersed in the corky layers of the bark. The economic recovery of the wax from waste product of the douglasfir lumber mills was undertaken by the Oregon Wood Chemical Company, Springfield, Oregon, in 1950.

The yield of wax from the bark ranges from 4 to 11 per cent, depending upon the richness of the raw material and the type of solvent used. The crude wax is of reddish-brown color, aromatic in odor, and firm in consistency, when extracted by hexane. The hardness by durometer is 83 at 24°C; its penetration value (100 g wt., # 14 needle, 25) is 8. A harder wax is produced by either ethyl ether or benzosol extraction of the bark. The extractive is light brown in color, and extremely hard in consistency, having a durometer hardness of 99 and a penetration value of 1. Although this wax is very hard it still had an unctuous feel. The wax of the bark may be extracted by other solvents, such as petrolic ether, benzene, benzene mixed with benzosol, diethylene chloride, and toluene. The three last-named solvents give the larger yields, with an optimum of 11.2 per cent, but the crude wax contains more of the resins, and phlobaphene.

The melting point of the crude wax is 55°C when extracted from the

bark by benzene, or 61°C if extracted by benzene from the lignin residue resulting from the treatment of sawmill waste by acid hydrolysis to recover sugars. The melting point of the wax extracted from the bark by ether is 62° minimum, 63°C maximum, by the Fisher-Johns melting point method. Kurth *et al.*[144], however, give the melting of the wax extracted from the ground bark by means of petrolic ether as 49°C (120°F). The product of the Oregon Wood Chemical Company which employs the latest Kurth process has a melting point of 60–63°C (140–145°F)[12].

Commercial douglasfir wax, produced on a pilot scale by the Solexol process at the M. W. Kellogg Company, is reported to have the following physical and chemical properties: melting point 163°F (72.8°C); penetration (100 g/77°F/0.1 mm) 1; specific gravity (d^{25}) 1.03, (d^{77}) 0.90, (d^{99}) 0.88; viscosity, 210°F, Saybolt seconds 97, centistokes 18.4; refractive index (Abbe) 176°F, 1.468; odor sweet, taste none; ash 0.09 per cent; acid value 35–45; saponification number 180–210; hydroxyl number 90; iodine number (Wijs) 12–20; volume decrease (Graef's formula) 13 per cent; hardness (Durometer) 77°F, 98. It has a solvent retention power (R.P.) 85–100 (comparates: slack wax 70–85, candelilla 40–50, esparto 30–40, carnauba 20–30, beeswax 10–20).

The hexane-insoluble wax (m. 60–63°C) of douglasfir bark has an acid value 74, saponification number 200–210, unsaponifiable 5–7 per cent, and methoxy (MeO) value of 5.43 per cent, according to Kurth and Kiefer[145].

Wax from Hydrolysed Mill Waste. Extractions of the douglasfir bark, of the wood-bark mixture used for hydrolysis at the Forest Products Laboratory, Madison, Wisconsin, and of the lignin residue from this hydrolysis were made by Clark *et al.*[54] with benzene on dry material, and with acetone on wet material. Where acetone was used the wax was extracted from the water-acetone extractives by benzene. These investigators utilized

TABLE 55. ANALYTICAL CONSTANTS OF DOUGLASFIR WAX

Specimen of Wax	Acid Value	Saponification Number	Ester Value	Iodine Number	Melting Point (°C)	Color
Bark—hexane extracted	80.7	189	108.3	62.5	61	brown
Bark—ethyl ether extracted[293]	58.6	160	101.4	44.7	62–63	light brown
Bark—petrolic ether extracted[144]	70.0	128	58.0	22.0	49	brown
Bark—benzosol extracted[54]	67.8	112	44.2	50.7	63	light brown
Hogged wood—bark benzene extracted[54]	46.1	176.8	130.7	42.3	53	brown
Lignin—benzene extracted[54]	74.2	170.4	96.2	27.8	61	black
Bark—benzene extracted[54]	46.8	194.9	146.1	37.4	55	brown
Refined lignin wax, petrolic ether-soluble	63.4	190.5	127.1	25.8	59	light brown

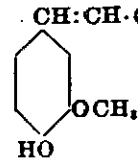
a waste from Springfield, Oregon, area; the waste consisted of mixed sapwood slabs with and without bark, the bark forming 30 per cent of the waste. It was ground in a Wiley mill through a $\frac{5}{64}$-inch mesh screen and oven-dried at 90°C to 0.9 per cent moisture; the benzene extraction was made from 5 kg of this mixture. For bark extractions the bark was stripped from slabs selected at random from the stock pile.

The lignin used for their work was the residual material from the diluted-acid hydrolysis of douglasfir waste material by the Madison wood-sugar process. The residue consists of 2.3 per cent of water-soluble matter, 6.5 per cent of benzene-soluble materials, 83.2 per cent of lignin, and 8 per cent of cellulose and other nonlignin matter. Extractions of the oven-dried hydrolysis-plant residue were made in a continuous-type Lloyd copper extractor; 28 liters of benzene were used for 8 kg of residue, and extraction was carried on for 50 hours to completion. At the end of the extraction the benzene was distilled from pot to outside receiver, and the concentrated wax solution was removed, filtered, and evaporated to dryness on a steam bath.

Clark *et al.*[54] determined the chemical characteristics of wax from hogged wood-bark, bark, and dried lignin residue. The values are given in Table 55. In addition they determined the acetyl values as 76.8, 80.6, and 77.6 respectively. The Reichert-Meissl values were 0.43, 0.14, and 6.7. The specific gravity (d^{20}) in each instance was 1.0500. The saponifiable wax material from douglasfir lignin amounted to 66 per cent. It melts at 69°C, and has a specific gravity (d_{20}^{20}) of 1.060, acid value 95.7, saponification number 203.3, ester value 107.6, iodine number 19.5, and R-M value of 0.24. The unsaponifiables are of a waxy nature, light brown in color, melt at 54°C, and have a specific gravity (d_{20}^{20}) of 0.980, acetyl value 95.8, and iodine number 30.5. They amounted to 22 per cent.

Van Beckum[293] extracted the whole bark with ethyl ether, distilled off the ether, and extracted the residue with hot water to remove water-solubles, such as mannose and gallic acid, the presence of the latter tending to darken the wax when it is melted. The water-insoluble material is a light-brown wax of very hard texture.

Chemical Composition of Douglasfir Wax. A wax extracted from douglasfir bark with hot benzene was separated into fractions soluble and insoluble in hexane by Kurth and Kiefer[145]. The hexane-soluble wax was light in color, hard, and had a melting point of 59–63°C. It consisted of about 20 per cent *lignoceryl alcohol*, 60 per cent *lignoceric acid*, and 20 per cent *ferulic acid* (4-hydroxy-3-methoxy-cinnamic acid). The hexane-insoluble wax was light brown to reddish brown, and had a melting point of 60–63°C. Extraction of wax-free bark with ethyl ether gave dihydroquercetin (m. 240–242°C).



ferulic acid

The wax from the bark, according to Van Beckum[238], contains acids with both hydroxyl (OH) and ketonic (CO) groups, and a small amount of glycerol. The hydroxy and keto acids of douglasfir have 10 carbons.

Clark *et al.*[54] saponified the wax obtained from douglasfir lignin residues, converted the saturated fatty acids to methyl esters, and then fractionally distilled the esters at 1 mm pressure. The C_{10}–C_{14} acids distilled at 100–152°C and amounted to 10.7 per cent. The following percentage amounts of other acids were obtained: C_{16-18}, 10.5; C_{20-22}, 13.7; C_{22-24}, 7.5 distilled at 190–191°C, 14.9 at 192–200°C, and 17.4 at 200–212°C. The undistillable residue amounted to 25.3 per cent and presumably consisted largely if not wholly of C_{26-28} and C_{30} acids (*n-melissic acid*). Glycerides are probably confined to those of acids below C_{20}.

Clark and co-workers found about one-third of the total fatty acids to have a resolidification point of 80.4–81.4°C, indicating a preponderance of *n-lignoceric acid*. The binary mixture of C_{20}–C_{22} acids resolidified at 77.2°C, and the C_{22}–C_{24} acids at 74.4°C; the predominating acid of these mixtures is the C_{22} acid (*n-behenic acid*). Melting points on acids lower than C_{20} were indefinite. Of the total acid fraction (65.6%), 27.9 per cent was heptane-insoluble, and of the 37.7 per cent heptane-soluble solids 9.6 per cent

TABLE 56. COMPOSITION OF DOUGLASFIR WAX*

Glycerides:	<1 per cent
C_{16}–C_{18} acids, including oleic	
Free Fatty Acids:	30 per cent
Saturated fatty acids	
Behenic acid	
Lignoceric acid	
Cerotic acid	
Aromatic Acids:	18–22 per cent[145b]
Ferulic acid (m. 170°C),[145b] free and combined	
Monohydric Alcohol Esters of Wax Acids:	45–50 per cent
Lignoceryl lignocerate, 40%	
C_{16}–C_{18} esters of C_{22}–C_{24} acids	
Phytosterols (m. 134–135°C), *free and combined:*	<1 per cent
Hydrocarbons:	<1.75 per cent
Phlobaphene and Resins:	>1 per cent

* Douglasfir wax extracted from bark by hexane, with yield of 3.8 to 6 per cent. Iodine number (Hanus) 18–22. Composition differs from that of wax obtained from douglasfir lignin residues.

consisted of unsaturated acids (ferulic? and oleic acids), and the remainder (28.1%) of saturated acids.

In the unsaponifiable fraction (22%) these investigators found 8.0 per cent hydrocarbons and 14.0 per cent alcohols. The water-soluble fraction which includes glucose amounted to 7.1 per cent and losses 5.3 per cent. The hydrocarbons were soft and indeterminate. The natural wax obviously undergoes some decomposition in hydrolysing the bark constituents with mineral acid, destroying the glycerides and affecting other changes. *Phytosterol* is a minor constituent of the wax. The acid constituents are present in both the free and combined states.

The chief unsaponifiable constituent is *lignoceryl alcohol*[12]. Next in importance is *behenyl alcohol*, and of least importance are *arachic alcohol* and *ceryl alcohol*. The higher iodine numbers for the wax extracted directly from the bark indicate the presence of *ferulic acid* in substantial quantity. Phlobaphene is a constituent of the wax and is responsible for its dark brown color. It has been estimated that about 80 pounds of wax could be recovered from a ton of dry lignin residue.

Uses of Douglasfir Wax. Clark and his associates[54] suggest the use of douglasfir wax in soap manufacture, for impreganting paper for waterproofing, and in emulsion polishes, leather dressings, metallic-soap lubricants and greases, carbon paper, and candles. Darker, high-melting fractions of the wax are suitable in a solvent medium as a parting agent for plastic molding. The "Chemurgic Digest"[12] reported that many uses have been found for the wax, including its use in polishes, ski wax, ointments, lubricants, soaps, art and sculpture work, preservatives, and the like.

Ocotillo Wax

Ocotillo (or ocotilla) wax is obtained from the bark of a succulent plant, known as *Fouquieria splendens* Engelmann, of the family Tamariscaceæ. The plant bears the provincial name of ocotillo, or coachwip cactus. Several species of these thorny shrubs[274] are commonly called candlewood. They grow in New Mexico, west Texas, southern California, and Mexico. *F. splendens* yields a gum generally known as ocotilla gum. The bark is said to yield 9 per cent of wax. A similar wax is derived from *Moquinia hypolenca* D.C., which grows on the banks of the Rio Grande. *M. hypolenca*, according to Lewkowitsch, yields 2 per cent of wax for the entire plant, the bulk of which is contained in the leaves; the stems and stalk yield only a small proportion.

For the extraction of the wax the ocotillo plant is dry heated until the moisture is driven out, whereupon a shellac-like gum separates from the wax; the wax is extracted by a suitable solvent such as benzin, and the solution evaporated to dryness.

Ocotillo wax melts at 84°C, has a specific gravity (d^{15}) of 0.984, and is soluble in alcohol and in benzene. Lewkowitsch determined its analytical constants: acid value 58.1; saponification number 185.0; unsaponifiable (m. 64–66°C) 43.1 per cent; fatty and wax acids (m. 60°C) 23.9 per cent. The wax is composed largely of an ester of melissyl alcohol (C_{31}) and carbocerotic acid (C_{27}), that is, *melissyl carbocerotate* (m. 86°C).

Little seems to be known of its uses. Its physical properties and chemical composition indicate that it might be exploited commercially if it were obtainable in sufficient amounts. Ocotilla gum has been used as a base for licorice chewing gum.

Wax of Oleander Bark

The sweet-scented oleander, *Nerium indicum* (*Nerium odorum* Aiton), family order Apocynaceæ, of India, yields an active principle known in Bengali as "karavi," a strong poison producing a powerful depression of the heart. The bark contains a wax of a peculiar composition. The wax was crystallized by Pendse and Dutt[206] from boiling absolute ethanol and appeared as colorless, glistening prisms possessing the following properties: melting point 97°C; density (d^{30}) 0.9804; saponification number 53.2; iodine number 16.2; acid value 16.8; and unsaponifiable matter 62.4 per cent. Hydrolysis of the wax gave an acid melting at 93–94°C (*cocceric acid*, m. 92–93°C), and an alcohol melting at 69°C (*carnaubyl alcohol*, m. 68–70°C). It hence appears to be *carnaubyl coccerate*. The leaves of the oleander are reported to contain *tetratriacontane*, $C_{34}H_{70}$, with a melting point of 70–71°C.

The leaves of *Nerium indicum* are reported to contain both *ursolic* and *oleanolic acids*. The foliage of the common oleander, *Nerium oleander* L., is reported to contain a white crystalline substance (m. 278°C) identified as *ursolic acid* and identical with that obtained from the leaves of *Uva ursi*.

Wax of the Mudar Bark

The stem bark of the Akund calotrope, *Calotropis gigantea* L., family order Asclepiadaceæ, which tree or shrub is called in northern India *mudar*, and in southern India, *yercum*, contains both resin and wax. Murti and Seshadri[196a] extracted the powdered, freshly dried root bark with ligroin, and then with ethyl ether to obtain 150 g of extractive from 4 kg of bark. The extractive when boiled with a liter of alcohol for three hours and then cooled to 60°C yielded a supernatant liquid, which when decanted from the insoluble viscous residue, containing mudarol (m. 176–177°C), deposited about 40 g of a white, waxy solid. This solid when recrystallized from alcohol and then from ethyl acetate, gave 20 g of a colorless wax with a melting point of 87°C. The yield is ½ per cent of the original weight of the

bark. The wax was found to consist of C_{31} and C_{32} hydrocarbons; fat acids C_{24} to C_{32}; β-amyrin (m. 180°C); β-amyrin isovalerate (acetate m. 238–239°C); and a little unidentifiable liquid fat acid. The unsaponifiable portion, a yellow wax, melts at 65°C, and at 69°C when recrystallized.

Wax is not only found in both stem and root barks of *C. gigantea* but in its latex. Most trees or shrubs with a milky juice, such as *Alstonia scholaris* L., of the East Indies, source of the alkaloidal dita bark of commerce, and many others, contain (besides lupeol-like compounds, α- and β-amyrins, and sterols) a small amount of wax which evidently is an associated end-product of their metabolism (see Waxes from Latex-bearing Plants, p. 267).

Olive-Bark Wax

The bark of the tropical-almond terminalia, *Buceras catappa* (L.) Lyons (*Terminalia catappa* L.), family order Combretaceæ, contains a small amount of wax. Power and Tutin[216] extracted the dried bark with alcohol and obtained 30 per cent of a lipid wax, which they found to consist chiefly of acids, alcohols, sterols, and hydrocarbons. The acids are monocarboxylic, namely, an acid $C_{35}H_{68}O_2$ (m. 69–70°C); an acid $C_{28}H_{46}O_2$ (m. 79°C); an acid $C_{35}H_{70}O_2$ (isoceroplastic ?, m. 92°C); and an acid $C_{30}H_{58}O_2$ (m. 84°C). The alcohols include a tertiary alcohol, $C_{35}H_{68}O$ (m. 70°C); an ordinary *sitosterol*, $C_{27}H_{46}O$ (m. 136°C, $[\alpha]_D$ −35.2°); a substance $C_{23}H_{38}O_2(OH)_2$ (m. 285–290°C) identical to *ipuranol*; *d*-mannitol; and sugar. A hydrocarbon, *pentatriacontane*, is also reported as a constituent.

It is of interest to note that olive-tree leaves, aside from *oleic acid* have *2-methyldocosanoic acid* (m. 68–69°C) as the acid component. The leaf contains several steroids: *oleasterol*, $C_{29}H_{34}O$ (m. 174°C), which is of a $C_nH_{2n-7}(OH)$ type; a crystalline hydroxyphytosterol, *oleastranol*, $C_{28}H_{42}O_2$ (m. 217–218°C); and *homolestranol*, $C_{27}H_{46}O_2$ (m. 210°C, $[\alpha]_D$ 78.3°C). The latter has one phenolic and one alcohol group. The leaf also contains the hydrocarbons, *hentriacontane* (m. 68–69°C), and *pentatriacontane* (m. 74—75°C).[216]

Wax of Cacao Husks

The unsaponifiable matter of the lipid fat from cacao husks, *Theobroma cacao* L., contains a waxy material which consists chiefly of N-petrolic ether-insoluble nitrogenous substances (m. 139.5°C and 115.3°C); *sitosterol*; *stigmasterol*; *amyrins*; *ceryl alcohol*; *nonacosane*; and a terpene.

Cocoa butter is the pure fat (not wax) extracted by pressure from the ground and crushed roasted cacao nibs. It is used in the manufacture of confectionary, cosmetics, and as a drug. Pure pressed cacao butter melts to a clear liquid at 33.0–35.8°C; has a refractive index ($n_D^{15.5}$) 1.449–1.451, ($n_{\ }^{40}$) 1.4570–1.4575; saponification number 192–203; iodine number 32.0–

37.6; R M number 6.6–8.4; thiocyanate number 32.7–34.9. Its specific gravity ($d_{15.5}^{15.5}$) is 0.950–0.975.

Cocoa butter contains 34.2–37.3 per cent of oleic acid glycerides, namely, oleodipalmitin and oleodistearin. The fatty acids consist of *palmitic*, 24.4; *stearic*, 34.5; *oleic*, 39.1; and *linoleic*, 2 per cent by weight. Cocoa butter contains only 2.5 per cent of fully saturated triglycerides. The highest iodine number of its liquid unsaturated acids is 103.1. It contains 3 to 13 mg per 100 g of tocopherol (vitamin E).

TABLE 57.

Plant	Alcohols	Sterols	Acids	Unidentified
Black locust (*Robinia pseudoacacia* L.)	Higher alcohol	Phytosterol	Palmitic Stearic Oleic	
Carob (St. Johnsbread) (*Ceratonia siliqua* L.)	—	—	Palmitic Stearic	
English hawthorne (*Crataegus oxyacantha* L.)	Ceryl	Phytosterol	Palmitic Stearic $C_{30}H_{42}O_6$* (m. 249°C)	$C_{30}H_{50}O$, or $C_{31}H_{50}O$ (lupeol)
European elm (*Ulmus campestris* L.)	—	$C_{27}H_{46}O$, H_2O (m.134°C) (sitosterol)	—	$(C_{12}H_{24}O)_n$ (m. 74–75°C) $C_{11}H_{20}O_2$ (decomp. 240°C)
European euonymus (*Euonymus europaeus* L.)	Ceryl	—	Palmitic Stearic	
Purpleosier willow *Salix purpurea* L.)	Ceryl	Phytosterol	Palmitic Stearic	A hydrocarbon
Red buckeye horsechestnut (*Pavia rubra* Lam.)	Ceryl	Sitosterol	—	A hydrocarbon
Norway Spruce (*Picea excelsa* L.)	Ceryl	—	Stearic Palmitic Juniperic	Lupeol? and other compounds
Planetree maple (*Acer pseudoplatanus* L.)	Ceryl	Phytosterol (crystalline)	Palmitic Stearic	—
Tree of heaven ailanthus (*Ailanthus altissima* Swingle)	Ceryl	—	Palmitic Stearic	A hydrocarbon

* Crategotrionic acid (a triterpenoid).

Note: In general the barks are extracted with petrolic ether and the alcohols isolated from the unsaponifiable, the acids being determined from the saponifiable. Many of the bark waxes undoubtedly contain amyrins; α-amyrin, β-amyrin, or lupeol, and carotenoids.

Waxy Matters in Miscellaneous Barks

The waxy constituents given in Table 57 were recorded by Zellner[329] and other investigators.

WAXES FROM LATEX-BEARING PLANTS

Latex-bearing plants such as the common dandelion (*Taraxacum officinale* Wiggers); yellow goatsbeard, known also as meadow salsify (*Tragopogon pratensis* L.); endive (*Cichorium endivia* L.); and common chicory (*Cichorium intybus* L.) contain minute amounts of wax, which is composed of *ceryl palmitate* and/or *ceryl stearate*, and free *ceryl alcohol*. The waxy extractive matter is generally accompanied by inositol and reducing substances.

Larger plants such as latex-bearing trees, *Brosimum* and *Clusia* species and the like, produce a considerable amount of sap which upon heating yields a coagulum accompanied by oily matter rich in wax content.

Cow Tree Wax

The name *cow tree wax* is given to the waxy material which separates from the thick milky sap of several species of trees, commonly known as the breadnut tree, milk tree, *pale de vaca*, and *arbol de leche*[274]. It is a species of *Brosimum*, family order Artocarpaceae, which consists of about eight species of trees with milky sap, indigenous to tropical America. One of these species, *B. alicastrum*, is found in Jamaica, where the seeds are called "breadnuts" and are esculent, the milk juice being acrid. Another species, *B. galactodendron* Don. [cow-brosimum (*G. utile* Kunth.)], is generally described as the source of the wax. The latex of this breadnut tree was separated by Justo Gomez into rubber, a wax melting at 64–65°C, and α-amyrin (m: 185°C), the same amyrin as that obtainable from gum elemi.

The cow tree wax derived from the tree growing in the north of Venezuela, near Lake Maracaibo, yields a wax which is marketed in Caracas. This species of cow tree has been referred to the genus *Clusia*, family order Guttaferaceæ, by a French botanist. There is one species of *Clusia* in the United States, *C. flava* Jacquemont, known as Key West *Clusia*, which has a resinous exudate which can be used like pitch. The *C. venezuelensis* tree yields a thick milk when incisions are made in the trunk. The milk when heated forms a skin; the skin is removed, and an oily liquid is obtained upon evaporation. When the oily liquid is solidified it yields a yellowish-white, hard, translucent wax. The wax softens at 40°C, melts at 50–52°C, but not completely at 60°C. It is saponified by potassium hydroxide; it dissolves readily in essential oils, and in boiling alcohol, but redeposits on cooling. The natives use cow tree wax as an ointment. The coagulated residuum of the latex is used in the manufacture of chewing gum. It is plastic at 37°C and brittle at lower temperatures.

The sap of the cow tree, *Tabernaemontana sphaerlcarpa* Bl., contains both α- and β-amyrins, as does also the sap of *T. utilis* Arn., of British Guiana.

Gondang Wax

Gondang-wax, or *cera fici*, is the lipid wax of a species of india rubber fig tree. The wax is also known as Godang, Kondang, Getah, and Java wax. The fig belongs to the family order Moraceæ, and there are about 650 species of the genus *Ficus* in the warm and tropical regions. The wax is obtained from the oil liquid which separates on warming the sap. The wax secured from the latex in Java is generally attributed to the variegated india rubber fig tree, *Ficus elastica variegata* Blume; that obtained in Sumatra and Ceylon to *F. ceriflua* Jungh, and is conceivably the same wax. One species, the white india rubber fig tree, *F. alba* Reiner, on coagulation of its latex yields much wax and little rubber. *F. elastica* Roxburgh, the latex source of East Indian rubber, contains a wax of a different kind. The saps of species other than those mentioned contain wax but not in appreciable quantities.

The cakes of gondang-wax are fairly hard, grayish-brown in color, yellowish-white inside, as prepared by heat treatment of the latex. They break with a conchoidal fracture but are scarcely friable. In its general character gondang-wax is intermediate between wax and caoutchouc. The crude wax melts at about 60°C to a very viscous mass which on cooling remains viscous for a long time, and some aqueous liquid separates out. The density (d^{15}) of the wax has been reported as 0.963 (Wiesner), or 1.0015 (Greshoff and Sack)[91]. It softens at 45°, melts at 56–57°, but is not completely melted at 73°C. It will solidify at about 51°C. The wax is soluble in benzene, chloroform, carbon disulfide, oil of turpentine, ligroin, and boiling alcohol.

When crude gondang-wax is remelted and dissolved in boiling alcohol, a purified wax product is deposited on cooling. This purer wax consists largely of a white crystalline solid which melts at 61°C. Greshoff and Sack[91] in 1901 determined its composition to be that of an ester, the alcohol component of which was a cylic compound (m. 197.5°C) they termed *ficoceryl alcohol*, and the acid component a straight-chain acid (m. 57°C) which they termed *ficoceric acid*. They also noted the presence of a substance in the alcohol-soluble portion which they regarded as an alcohol, possibly related to ficoceryl alcohol.

Ultée[289] in 1915 examined the sap of the variegated india rubber fig tree, *F. elastica variegata*, and found the ficoceryl alcohol constituent of Greshoff and Sack[91] to be identical with β-amyrin [$C_{30}H_{49}OH$, m. 197.3°C, $[\alpha]_D^{20}$ 87.35°]. To prepare the resinol the sap is coagulated by warming or the

addition of alcohol, and the wax extracted repeatedly with large volumes of boiling alcohol. From this a product settles out which when saponified yields an alcohol having all the characteristics of β-amyrin. The substance soluble in cold alcohol, which Greshoff and Sack regarded as similar to ficoceryl alcohol, is now believed to be *lupeol*. When the alcohol is treated with acetic anhydride, lupeol acetate [$C_{32}H_{52}O_2$, m. 214°C, $[\alpha]_D^{20}$ 43.3°] is obtained. Lupeol, according to the Vesterbergs[304], has the formula $C_{30}H_{50}O$ and not $C_{31}H_{50}O$ (m. 212–213°C) as assigned by Dieterle[68] to the constituent he isolated from the husks of lupine seeds.

In 1924 Ultée[290] concluded that the ficoceric acid of Greshoff and Sack is in reality *palmitic acid*, and the wax is chiefly β-amyrin-palmitate. The natural wax melts at 69.5°C, whereas the synthetic ester prepared from β-amyrin and palmityl chloride melts at 77°C.

Ultée[291] in 1922 reported that the latex of the tawny fig, *Ficus fulva* Reiner, which contains much wax and little rubber, yielded *stearic acid* on hydrolysis. Ultée[292] also reported that the wax derived from the coagulation of the white fig, *F. alba* Rein., has a melting point of 60°C. On hydrolysis the wax yielded *stearic acid*, β-amyrin, and lupeol. The β-amyrin was isolated free and in the form of acetate, and the lupeol as benzoate.

Gondang wax is used as a candle material in Java and Sumatra.

Wax of Milkweed

Kurtz, Jr.[146], of the University of Arizona, Tuscon, in 1950 extracted 1.26 per cent of wax from a species of milkweed, *Asclepias linaria*. The plant was dried and extracted with petrolic ether, and the extract separated into wax and nonwax fractions with acetone. The amount of wax ester and wax acid constituents was found to increase with the age of the plant. The latex of the common milkweed (or silkweed) *A. syriaca* L., contains both α- and β-amyrins.

Wax of Guayule

It has been reported by the U. S. Natural Rubber Research Station, Salina, California, that the guayule plant, *Parthenium argentatum*, contains wax in the phloem above the crown and in the actively growing parts, and that the wax is constant in shrubs of the same age and variety harvested at different seasons.

WAXES FROM FRUITS AND BERRIES

Although a berry is a fleshy fruit which does not open (indehiscent), the seeds being embedded in the flesh (sarcocarp), it is commonly distinguished from the larger, fleshy, indihiscent (baccate) fruits of firm and hard kind, only by its very small size and thin rind. A number of species of

berries are thinly coated with a natural wax having a high *ursolic acid* content, e.g., the cowberry, *Vaccinium vitas-idaea* L., and Old World species, which is also called the Mount Ida whortleberry. The ursolic acid isolated from the cowberry has a melting point of 273–274°C, recrystallized from ethanol at 282–283°C, which is raised to 285–288°C by repeated crystallization after purification through its potassium salt. Another example is the wax derived from the rind of the cranberry, *Vaccinium macrocarpum* Aiton (see Cranberry Wax, p. 282).

The large-size fruits, mostly cultivated, like those of the *Citrus* tribe (Aurantiaceae) and the deciduous fruits such as the apple and pear, have a very thin coating of wax on the pericarp, e.g., the apple (see Apple Skin Wax, p. 288).

Classed as wax-producing, but not yielding true natural waxes, are a number of berries which furnish a vegetable tallow (glycerides) that is of a waxlike consistency, e.g., the wax myrtle, *Myrica cerifera*, and the bayberry, *Myrica pensylvatica*. These tallows are commonly classed as waxes since they find similar uses in the arts and industries, and blend readily with true natural waxes and paraffins.

Japanwax

Japanwax, or japan wax, may be defined as a vegetable tallow derived from the seed of certain species of *Toxicodendron* Mill. (*Rhus* L.). It is not a true wax since it contains too large a proportion of glycerides to be so classified. The tallow is found between the kernel and outer skin (mesocarp) of the berries (fruit) of the "waxtree," a small sumac tree, distinct from true sumacs (*Rhus*). *T. succedaneum* (*Rhus succedanea* L.), var. *Doumoutiere* (Kudo and Matuura), otherwise known as *Annam urusi*, is cultivated in Annam, French Indo-China, for the tallow (japanwax) it yields (ca. 7.5%).

Japanwax is also derived from other species of Toxicodendron, such as *T. vernicifluum* (*R. vernicifera* D.C., the so-called Japanese lacquertree; or from *T. trichocarpum* (*R. trichocarpa* Shiina), the peelberry poison sumac, grown in China, Indo-China, India, and Japan. The berry is of the size and shape of the common white bean, and the wax occurs as a greenish coating on the kernels.

In Japan *T. succedaneum* is known as *yama-hazi*, and *T. vernicifluum* as *uroshinoki*, or the *lacquer plant*. The latter is the taller tree and is 20 to 30 feet high. It begins to bear fruit at 15 years, and continues to do so for over a hundred years, yielding 30 to 150 pounds of berries, or nuts, per year. Since the trees are cultivated for the sake of the lacquer they exude, japanwax in a sense might be considered as a by-product of the lacquer industry in the Orient. The principal production region of japanwax is in the island of Kyushu[8].

The procedure for producing the wax from the waxtree has been recorded as follows. The berries or nuts are gathered, dried, and crushed, and the kernel separated from its pericarp by winnowing. The kernels are steamed and placed in hempen cloth bags, steamed again, and pressed in a wooden wedge press. The yield is 15 per cent or more of a coarse, greenish, tallowy mass. In the pressing, the flow of the last portion of wax is sometimes accelerated by the addition of a little perilla oil. The crude wax, solidifying at 50°C, is cast into round molds holding one pound each.

Decolorizing Japanwax. In the customary refining, the wax is mixed with decolorizing carbon of vegetable origin, and water, and boiled thoroughly. The molten wax is then poured into cold water to form "wax flowers." The yield is about 10 per cent of the original weight of the berries. The wax flowers are skimmed off, and exposed to the sun for about 20 days; the process of making flowers and sunning is repeated, and the wax is remelted and cast into cakes. It is very white and opaque, and differs from other white waxes in opacity and freedom from gloss.

An expedient method of bleaching japanwax has been sought for over a score of years, and is still a subject of investigation. One of the many methods proposed for bleaching japanwax involves emulsification of the melted wax with aqueous sodium hydroxide and hydrogen peroxide, coagulating the wax by pouring it into cold water, and then exposing it to ultraviolet light.

Physical Characteristics of Japanwax. The purified wax which has not received the repeated sun-bleaching comes into the market in straw-yellow flat cakes, discs or squares. The pigment can be removed by extraction with 95 per cent ethanol. Japanwax ordinarily is unctuous to the feel and somewhat rancid in odor like animal tallow; it also has a rancid taste. Under ordinary circumstances it fuses at 51 to 55°C, but a recently solidified sample melts at a lower temperature. Its solidifying point is about 41°C; the temperature rises to 48° or 49°C in the act of solidification.

The specific gravity (d^{15}) of japanwax is 0.975–0.993 when solid, and when melted (d_{15}^{98}) 0.875–0.877. Thus japanwax in the solid state has a density similar to that of a true wax, but in the molten state it is heavier than a true wax—a general characteristic of a vegetable tallow. Kleinstück found that the density of japanwax approximates that of water at certain temperatures, and coupled with a high coefficient of expansion, gives rise to the peculiar phenomenon of its floating in water at about 18°C and sinking below 15°C. He found the density (d_4^t) to be 1.0074 at 7.2°C, 0.9985 at 17.5°C, and 0.9862 at 26.5°C.

Japanwax of commerce is a medium hard, pale ivory colored wax; it gives a penetrometer reading (# 14 needle, 100 g/20 sec/25°C) of 23, in contrast to that of paraffine (128/130°F—A.M.P.) which is 37–38. Its

durometer hardness is 70. However, specimens of japanwax several years old appeared to be softer and give higher penetration values. The Fisher-Johns melting point of japanwax is 45°C (113°F) minimum, 51°C (123.8°F) bulk, and 53°C maximum. A specimen several years old gave an F-J melting point of 42°C minimum, 48–48.5°C bulk, and 48.5–49.5°C.

The chemical constants of japanwax are as follows: acid value 6–20, saponification number 206.5–237.5, iodine number 4.5–12.5, acetyl number 26.5–31.5, and Hehner number 90–91. The combined fatty acids have a melting point (drip) of 56–62°C, and a titer of 58–59°C. The nonsaponifiables constitute only 1.1 to 1.6 per cent of the wax.

Chemical Composition of Japanwax. The chemical composition of japanwax has been the subject of unending study. The composition primarily is that of a vegetable tallow, namely glycerides of fatty acids, chiefly *palmitin*. Japanwax differs from other vegetable tallows in that it contains a proportion of dicarboxylic acids, which have been referred to as "japanic acids." Tsujimoto[231] in 1935 contended that these dibasic acids occur in the unbleached wax as mixed glycerides of both japanic and oleic acids; and to the extent of 5.2–6.3 per cent on the dibasic acid basis. It is known that the dibasic acids are changed or lost to an appreciable extent in the refining.

In 1907 Schaal[242] had reported on his study of the constituents of japanwax in which he hydrolysed and distilled off the free fatty acids, then fractionated the undistilled portion, not volatile at 250 and 15 mm pressure, in the vacuum of a cathode light. He obtained in this way dicarboxylic acids of high molecular weight which he proceeded to identify. These acids are *α,ω-nonadecanedioic* (heptadecamethylenedicarboxylic acid), $HOOC\cdot(CH_2)_{17}\cdot COOH$; *α,ω-eicosanedioic*, $HOOC\cdot(CH_2)_{18}\cdot COOH$; and *α,ω-heneicosanedioic*, $HOOC\cdot(CH_2)_{19}\cdot COOH$, the latter being specifically termed by Beilstein as *japanic acid*. In 1931 Tsujimoto[230], making use of the difficult solubility of the dibasic acids obtained from unbleached wax of the *Rhus succedanea*, isolated dicarboxylic acids of a higher formula weight than those of Schaal, namely the C_{22} acid, *docosanedioic* (m. 125.7–126.3°C, Sitiro Siina) and the C_{23} acid, *tricosanedioic*, which melts at 123.5°C.

In 1911 Tassily[271] reported that japanwax consists principally of *palmitin* and free *palmitic acid*; there is also present *japanic acid* and its two lower homologs, as well as small amounts of soluble monobasic acids, inclusive of *pelargonic acid*, $C_9H_{18}O_2$, or *n*-nonanoic acid. The origin of japanic acid and pelargonic acids is possibly brought about by disruptive oxidation of tricontenoic acid in the plant metabolism. Tassily reported the presence of a C_{14} acid which was not identified, and very small amounts of *oleic* and *stearic acids*, but no arachidic.

In 1935 Tsujimoto[231] gave the component parts of the fat acids obtained

from unbleached wax of *T. succedaneum*, free from kernel oil, as 77 per cent *palmitic*, 5 per cent *stearic* plus *arachidic*, 12 per cent *oleic*, a trace of *linoleic*, and 6 per cent of *dicarboxylic acids*. He distinguishes the amount of dicarboxylic acids found in two types of wax as 6.2 per cent in *tsuta-urushi* and but 1.6 per cent in *yamahazi* (*T. succedaneum*). In 1944 Shichiro Shiina[250] reported that he had isolated both *eicosanedioic* [$HOOC(CH_2)_{18}COOH$] and *docosanedioic* [$HOOC(CH_2)_{20}COOH$] acids from Chinese urushi (*T. vernicifera*) wax, and in 1946 these same acids were found in the seed of *T. succedanea*, produced in Annan, French Indo-China. He also isolated the C_{22} acid from the seed of *T. trichocarpum*. These investigators stated that the wax from the seed of *nurude*, a kind of urushi tree, does not contain dibasic acids, but does contain a small amount of *lignocerin*, in addition to *palmitin*, its chief constituent. In 1930 Flaschenträger and Halle[80] reported the presence of a C_{23} dicarboxylic acid which they estimated as 0.3 per cent in the bleached japanwax.

Japanwax contains 10 to 14 per cent of glycerol, almost entirely in the combined state as palmitin, stearin, olein, and glycerides of dicarboxylic acids. The high acetylation number indicates the presence of free alcohols inclusive of some glycerol. Matthes and Heintz[183] studied the unsaponifiable insoluble matter of japanwax, and obtained 60 per cent of oxygenated liquid products; myricyl alcohol (m. 88°C); phytosterol (m. 139°C) with a double linkage (probably β sitosterol); ceryl alcohol (m. 79°C); and a saturated alcohol (m. 65°C) which apparently is *arachic alcohol*.

From the mesocarp of the fruit of *Annam urusi*, *Toxicodendron succedanea* L. [var. *Dumoutiere* (Kudo and Matuura)], was obtained 7.54 per cent of solid tallow by ether extraction. Hata and Kunisaki[98a] in 1940 reported that the solid fat has a high viscosity and a melting point of 54–55°C, and resembles vegetable wax. It consists of *palmitin* 82 per cent, *oleic acid* 8 per cent, *stearic acid* 4 per cent, *lignoceric acid* 2 per cent, *heneicosanedioic acid* 2 per cent, and small amounts of *tetradecenoic* and *hexadecenoic acids*. The unsaponifiable substances comprise principally *myricyl alcohol* and *sitosterol*.

In 1942 Ueno and Tsuchikawa[236a] reported that japanwax contained 66 per cent of C_{16} and 23.6 per cent of C_{18} monobasic acids, and 4.7 per cent of dibasic acids.

The approximate composition of japanwax based upon its chemical constants and our present knowledge of its constituents is given in Table 58.

Uses of Japanwax. Japanwax in the crude state, often an unbleached greenish-colored wax, admixed with a considerable amount of paraffin, is used in the manufacture of candles which are sold for burning in the temples and houses in Japan. The wax at one time was imported in large

TABLE 58. APPROXIMATE COMPOSITION OF JAPANWAX

Glycerides of Monobasic Acids:	90–91 per cent
Saturated simple glycerides of monobasic acids:	
Palmitin, 76–82%	
Stearin, 4–6%	
Arachidin and lignocerin, 2–3%	
Unsaturated simple glycerides of monobasic acids:	
Olein (4–8%) and linolein (trace)	
Glycerides of Dibasic Acids:	3–6.5 per cent
Simple glycerides:	
of nonadecanedioic acid (C_{19})	
of japanic acid (C_{21}), 1%, Schaal	
of tricosanedioic acid (C_{23}), 0.3%	
Mixed glycerides of dibasic and oleic acids:	
of eicosanedioic acid (C_{20})*	
of docosanedioic acid (C_{22})*	
Free Fatty Acids:	3.7–5.6 per cent
Soluble fatty acids: pelargonic ($C_9H_{18}O_2$)	
Insoluble fatty acids: palmitic, oleic, and α-linoleic acid	
Free Alcohols:	1.2–1.6 per cent
Monohydric aliphatic:	
Arachic (m. 66°C), ceryl (m. 79°C), and myricyl alcohol (m. 88°C)	
Glycerol	
Sterols: β-sitosterol, $C_{27}H_{45}(OH)$, (m. 139°C), 0.7%	

* Little is known concerning the proportion of C_{20} and C_{22} dibasic acids nor the extent to which they are mixed with oleic acid.

tonnages from Japan and used as an activating agent in the vulcanization of rubber; in recent years it has been too expensive for that purpose. Because of its large saponifiable content japanwax was at one time (about 1916) used in Germany in the manufacture of soaps; the wax constituted ⅓ to ⅔ of the soap stock; glycerol was obtained as a by-product. Japanwax has been used in the manufacture of polishes, pomades, and leather dressing. It is still an indispensible ingredient in the manufacture of graphite lead pencils.

Japanwax is of value to commercial laundries where it is worked with starch to produce flexible starched fabrics. It is used as a sizing material or slip for cordage. For many purposes for which waxes in general are used we find japanwax entirely unsuitable, because it is too fatty and too easily hydrolysed. Japanwax makes an excellent base for emulsifiable softening agents in finishing textiles. The dibasic acid constituents of japanwax, namely *japanic acid* and its homologs, have remarkably good softening value when applied to various fibers, and the glycerides of such dibasic acids are superior to the wax itself as fiber-softening material, as well as a polishing material for wood furniture and leather products.

Commercial Application of Dicarboxylic Acids. The application of higher dicarboxylic acids to the textile and varnish industry has been described by Shiina[249]. He has also pointed out the superiority of the triglyceride of eicosanedioic acid, $HOOC\cdot(CH_2)_{18}\cdot COOH$, over japanwax as a polishing material for wood furniture and leather products. A mixture of docosanedioic and eicosanedioic acids is easier to obtain from japanwax than are the two acids separately, and the glyceride of this mixture is a satisfactory and desirable material for used in the textile industry to soften fibers. It is necessary prior to use to convert the dibasic acids largely to glyceride and treat the various fibers with an alcoholic solution of the acid and glyceride.

The available supply of japanwax except for war years has always been abundant, but the demand has greatly increased within recent years and World War II created an acute shortage. The textile industries in the United States have been very large users. About 3000 tons of japanwax are produced normally each year in China, and somewhat over twice that amount in Japan. Japanwax imported by the United States has come out of Kobe. The price of the wax in 1950 was 62–65 cents per pound. In Japan the unbleached japanwax is used in the manufacture of candles since it gives little smoke in burning.

Myrica Waxes

Bayberry Wax. Bayberry wax is a waxlike fat (vegetable tallow) derived from the fruit coat of the bayberry, or wax myrtle, *Myrica cerifera* L., or closely allied species, such as *M. caroliniensis* K. & D. (*M. pensylvanica* Louiseleur), and *M. californica*, the "Pacific wax myrtle." *M. caroliniensis* Miller is now regarded as the same species as *M. cerifera* and is commonly referred to as "wax myrtle," the *M. pensylvanica* as "northern bayberry." Kelsey and Dayton[123] state with respect to the latter that "this more northern, seashore, deciduous species is frequently confused with *M. cerifera*, which gets no further than New Jersey, and has narrower, evergreen, sharp tipped and less pubescent leaves, and smaller berries." *M. cerifera* grows from Maryland to Florida, west to Texas and Arkansas. The shrub is sometimes provincially called candleberry, candleberry myrtle, tallowberry, and waxberry. *M. pensylvanica* inhabits the eastern coast from Canada to Florida, more particularly the coast of New England.

The bayberry shrub grows 4 to 8 feet in height; the ripe drupes are separated, globous, bluish-white in color and very waxy. The slender leaves of the *M. cerifera* are 2 to 2½ inches long, have minute, resinous, reddish dots on both sides, and are very fragrant when rubbed; the drupe grows in clusters less than one inch in diameter, the berries being attached singly or in clusters close to the stem. The plant grows in dry or moist sandy soil.

M. pensylwanica, or the northern bayberry, has a broader leaf, 2 inches long and ½ inch in width, and is without serrations. The berries are in clusters of four to six, and less close to the stem. They are larger and yield more wax than those of *M. cerifera*. A hybrid of *M. pensylvanica* and *M. cerifera* also exists.

To prepare the bayberry wax the berries are gathered from the shrubs and boiled with water; the wax melting and floating on the surface is skimmed off and strained, or allowed to concrete as the liquor cools, and then removed. The wax is purified by remelting and straining before it is cast into cakes. Much of the bayberry wax of commerce is produced in the New England States and also used there in the manufacture of Christmas candles. The industry is not entirely free from the unscrupulous practise of adulterating the bayberry wax with paraffin wax.

A specimen of bayberries collected by the author along the sand dunes between Wildwood and Cape May, New Jersey, during the month of August yielded 8 per cent of clean wax after boiling the berries in water for 10 minutes. Bayberries collected at Cape Cod, Massachusetts, in September yielded 11 per cent of wax. The wax is of apple grayish-green color, somewhat diaphanous, more brittle and unctuous to the touch than refined beeswax, of a pleasant aromatic odor, and of slightly bitterish taste. The water in which the berries are boiled becomes wine-red in color, and fragrant in odor.

The wax of M. cerifera (*M. caroliniensis* Mill.) had a density of 0.9853 at 15°C, and 0.9775 at 25°C; it melted at 44.8°C (112.5°F); density of melt (d^{98}) was 0.8780. It had an acid value 3.52, saponification number 208.0, an ester value 204.48, and iodine number (Hanus) 2.93. The Fisher-Johns melting point of a specimen of Cape May bayberry wax after one year of aging was 43–43.5°C minimum, 45–45.5°C bulk, and 51–52.5°C maximum. The wax increases in melting point on aging.

Smith and Wade[255] reported the following characteristics for bayberry wax (*M. cerifera*): specific gravity 0.9806 at 22°/15.5°C, 0.875 at 99°/15.5°C; melting point 48°C; softening point 45°C; saponification number 217; iodine number (Hübl) 3.9; Reichert-Meissl number 0.5; and index of refraction (n_D^{80}) 1.4363.

No information appears to be readily available concerning the chemical and physical characteristics of the wax obtained from the Sierra wax myrtle, *M. hartwegi*, found in the Sierra Nevada mountains; or of the Pacific waxy myrtle, *M. californica*, a large evergreen shrub with resinous wax-covered fruit, that grows along the coast from Los Angeles to Washington.

McKay[185] of Queens University, Kingston, Ontario, Canada, examined a bayberry wax (*M. pensylvanica*?) with an iodine number of 0, and of

46–49°C melting point, for its chemical composition. From 102 g he separated 95 g of fatty acids (100 per cent yield), which he refluxed with methanol containing 5 per cent of sulfuric acid, and fractionated the resulting methyl esters by distillation at 29–30 mm pressure. This investigator obtained 24.8 g of methyl myristate (m. 17.8°C); 3.32 g of methyl palmitate (m. 27.2°C); and 9.6 g of methyl stearate (m. 34.6°C). After further purification these esters gave melting points of 18.58, 29.6, and 38.35°C respectively. Upon saponification of the methyl esters followed by acid hydrolysis, McKay found *myristic acid* (m. 54.9°C), palmitic acid (m. 63.0°C), and stearic acid, (m. 69.8°C) as the fatty acid constituents. The chief components of bayberry wax are therefore, *trimyristic*, *tristearin*, and *tripalmitin* in the order named.

The wax of the wax myrtle, *M. cerifera*, is generally believed to consist entirely of *trimyristin*. The chemical composition as set forth by McKay indicates that the more northern and harder bayberry waxes contain a considerable amount of the higher glycerides (probably mixed glycerides) which in turn are reflected in the higher melting points.

Myrtle Wax. Myrtle wax produced in Central and South America is extracted from the berries of the *Myrica arguta* Kunth and related species, when they have matured to a light-gray color, at which time the wax is most yellowish in color. The hard coating is removed from the berries by boiling them in water and skimming the wax rising to the surface. The wax melts at 45°C. The fatty acids solidify at 46.4°C. The constants reported are: acid value 4.5, saponification number 216.7, iodine number 1.03, unsaponifiable 0.4 per cent, ash 0.06 per cent, and moisture 0.31 per cent.

Myrtle wax produced in Mexico is extracted from the berries of *Myrica jalapensis* Kunth and *M. xalapensis* H.B.K. The berries are reported to contain 7 to 12 per cent of greenish-white wax extractable by boiling water. They are collected by Indians from the plants which grow in dense thickets covering considerable areas in Veracruz, and the wax is marketed in Mexico City. Mexican myrtle wax, the Spanish name of which is *arbol del cera*, melts at 43°C, but upon long exposure the melting point rises to 47.5°C. A specimen from Tepic, Mexico, was greenish-white, another from Hidalgo greenish-yellow in color. The wax can be dispersed in 20 parts of hot water, but most of the wax deposits on cooling. It is soluble in most organic solvents and is easily saponified. Olsson-Seffer[202] has reported the following constants for Jalapa myrtle wax: melting point 43.2°C, density (d^{99}) 0.8763; acid value 4.17; saponification number 214.5; and iodine number 2.38. Arbol del cera (arbol wax) is the name by which the wax is sold in Mexico.

There is little difference between so-called myrtle wax and bayberry wax, in either physical characteristics or chemical composition. Myrtle

wax, capberry wax, and bayberry wax might well be classed under the general heading of "Myrica Waxes."

Capeberry Wax. Capeberry wax is in reality a vegetable tallow; it is derived from *Myrica cordifolia*, a bush growing on the sand drifts between Port Elizabeth and Cape Town[221]. The wax has very similar characteristics to bayberry wax from which it differs but little in composition. The wax is obtained by boiling the fruit in water. Capeberry wax as described by Schoeman and Hawke[243] is hard, greenish-white to green, with a smooth glossy surface and an herb-like odor. Solvent extraction gives a darker and less saturated product.

Rindl[221] stated that "berry wax" in South Africa is obtained from more than one species of *Myrica* or wax myrtle, and has recorded variations in five samples of capeberry wax: melting point 40.5–45.0°C, density (d^{15}) 1.004–1.007, saponification number 211–214.6, iodine number 0–2.38, mean molecular weight of fatty acids 236.1. Thorpe[274] previously recorded the analytical constants of a myrica wax growing in Cape Colony, South Africa, as specific gravity (d_{15}^{99}) 0.874, melting point 40.5°C, acid value 2.5, saponification number 212, iodine number 2.0, unsaponifiable 2.5 per cent. The wax was said to be derived from *M. quercifolia* (ostensibly the same as *M. xalapensis*), and possessed a grayish-green color.

In 1948 Schoeman and Hawke[243] reported the following constants for the wax derived from the fruit coat of *M. cordifolia*: melting point 40–40.7°C, density (d^{15}) 1.004, refractive index (n_D^{45}) 1.4504, titer 46, acid value 3.69, saponification number 214.7, iodine number 0.6, acetyl value 68.2, Polenski number 2.3, Reichert-Meissl number 0.5, unsaponifiable 0.12 per cent, fatty acids 90.4 per cent, glycerol 15.2 per cent. These investigators give the composition of the fatty acids (m. 47.5°C) as: lauric 0.3, myristic 47.0, palmitic 51.8, stearic 0.3, unsaturated (as oleic) 0.6; mean molecular weight 243.1. It would appear that capeberry wax has a greater proportion of *tripalmitin* and less *trimyristin* and *tristearin* than bayberry wax.

Commercial Myrica Waxes. The name "myrtle wax" has in the past been erroneously given to the myrica waxes. The shrub known as myrtle belongs to the family order Myrtaceae and not Myricaceae. Some of the commercial waxes, particularly those which sell at a very low price, are of doubtful purity. The density of the commercial waxes is generally recorded as 0.9995–1.0262 at 15°C, and 0.975–1.098 at 25°/15°C. Pure bayberry wax has a density closer to the lower of these limits. The melting point is reported as 40.5–48°C; it is known to increase with the aging of the wax. A specimen of bayberry wax prepared from berries collected at Wildwood, New Jersey, increased from 45° to 60°C in melting point in the course of ten years, with an indicated partial loss of its glycerol component. Its lowest glyceride component melted at 53°C.

The index of refraction of myrica waxes is reported as 1.4360–1.4363 at

80°C. Acid values of 2.5 to 21.2 have been reported; the higher value is that of a very old rancid wax, or implies adulteration with stearine. The acid value should not exceed 4.0 for a reasonably fresh wax. The iodine number ranges between 1.03 and 3.9, but should not exceed 3.0. The saponification number for unadulterated myrica waxes is quite constant, ranging from 205 to 217, with the mean at 213.

Myrica waxes have been of value in medicine, particularly in Mexico. Under the name of "arbol del cera" the wax has been used by the natives for treatment of diarrhea and jaundice. In dysentery the wax is used in a powdered form as a remedy[293]. Myrica waxes are sometimes used as substitutes for beeswax in the formation of plasters prepared by the apothecary.

The principal use of the myrica waxes in South Africa and in America is in the manufacture of very high-grade candles and tapers. Highly decorative candles suited for Christmas and other festive occasions are regularly made from these waxes today, as they were in the days of the Pilgrim Fathers in New England. Bayberry candles emit a fragrant odor when burning although the light is less brilliant than that obtained from common lamp oil. Myrica waxes give a splendid quality soap of white color, but the price is prohibitive for such use.

Wax of Mistletoe Berries

The white globous berries of the European mistletoe, *Viscum album* L., have a deposit of wax in the cutinized layers of the epidermis, which causes water to flow over the cuticle without being absorbed. From the petrolic ether extract of commercial bird-lime made from mistletoe berries the hydrocarbon *triacontane* (m. 65°C) has been isolated, and also *ceryl alcohol*. *Myricyl alcohol* and a *sapogen* have been isolated from the mistletoe by other investigators. Winterstein and Hämmerlee[322b] in 1931 reported that they had obtained 1–2 per cent of a sapogen from mistletoe (*V. album*) and which was not identical with *ursen*, claimed by van Itallie, but with *oleanolic acid* of olive leaves. It is a pentacyclic unsaturated monohydroxy-monocarboxylic acid of the formula $C_{31}H_{50}O_3$ (m. 306–308°C). It forms an acetyl derivative (m. 258–260°C) and a methyl ester (m. 196–198°C) which is saponified with difficulty. Oleanolic acid is also found in the blossoms of the marigold, *Calendula officinalis* L. Van Itallie in 1921 had reported the sapogenin to be ursen (m. 287°C) but noted that its melting point was higher than that of the ursen of Noogen (m. 272–274°C). The latter has the empirical formula $(C_{10}H_{16}O)_3$, with a molecular weight of 456.68. Oleanolic acid belongs to the β-amyrin group, and the formula $C_{30}H_{48}O_3$ is usually assigned to it in preference to $C_{31}H_{50}O_3$. The wax of the mistletoe also contains *stearic*, *palmitic*, *myristic*, and possibly *arachidic acid*.

The berries yield 5–6 per cent of extractives with petrolic ether, and the

extractives contain a resin alcohol, *viscresinol*, $C_{15}H_{26}O_2$, and a wax alcohol (m. 71°C) named *loranthyl alcohol*. The latter has the composition $C_{24}H_{50}O$, and is probably an isomer of lignoceryl alcohol. It is interesting to note that bird-lime prepared from the drupes of the European holly (*Ilex aquifolium* L.) contains a sapogenic acid (ostensible *oleanolic*, and the steroid, α-amyrin (m. 181°C), the latter as *α-amyrin palmitate*.

Yatara Obata of the University of Tokyo isolated the acid constituents of the resin wax of the woody portion of mistletoe, parasitic on Mongolian oak, *Quercus crispula*, and identified *oleanolic acid* as the resin acid, and *palmitic*, cerotic, linoleic, and linolenic acids as the fat acids [*Chem. Abstracts*, **45**, 3912 (1941)].

Wax of Serviceberries

In the treatment of the ether extract of the dried residue obtained after alcoholic extraction of ripe serviceberries with methanol-petrolic ether (1:1), an insoluble waxlike substance was precipitated. The serviceberries, European mountain ash, *Sorbus aucuparia* L., were collected in the neighborhood of Oslohas, Norway, by the investigator, Jermstad[119c]. The wax was saponified with alcoholic potassium hydroxide and benzene. The unsaponifiable was found to contain an alcohol (m. 78°C), a higher homolog of ceryl alcohol. A formula $C_{34}H_{70}O$ was assigned to the alcohol, which they called *sorbol*. It was believed to be an isomer of the normal C_{34} alcohol, but not identical to the C_{34} isomer isolated from humblebee or cotton wax, or from the fat of *Thuja occidentalis*. The acid component of the wax was not identified. The wax contains carotenoids.

Wax of Raspberry

Some of the fruit waxes are of academic interest only, such as the wax of the raspberry, *Rubus* spp. It was first separated from the settlings of raspberry oil by Marcelet [*Compt. rend.*, **204**, 1446 (1937)]. It comprised 22.8 per cent of the unsaponifiable constituent of the oil itself. He isolated from the unsaponifiable an alcohol $C_{19}H_{40}O$ (m. 62.5°C), which corresponds to *nonadecyl alcohol* (m. 63°C).

Cochin-China Wax

A product from the fruit of the cay-cay tree growing in the Far East is often listed under waxes, just as is myrtle wax, although both are very largely glycerides of myristic acid or its homologs, and are properly termed "vegetable tallows." Cochin-China wax has about the consistency of myrtle wax. The fruit of both *Irvingia oliveri* Pierre and *Irvingia malayana* Oliver, the latter of Cambodia, yield a wax, the preparation of which will be described later.

Closely allied to Cochin-China wax is the product "Dika butter" derived from *Irvingia barteri* Hook and *Irvingia gabonensis* Baillon, both indigenous to Nigeria. The tree which yields Cochin-China wax is a forest tree growing to a height of 100 feet, and belongs to the family Simarubaceæ. The fruit is the size of a lemon, with a kernel the size and shape of an almond, and ripens in July, when it falls to the ground. The *I. gabonensis*, a similar tree, is found in West Africa from Sierra Leone to Gabun, and is known as the "iba-tree" or African mango tree. Its fruit, a stone one, has been described by Grimme[92] as being the size of a swan's egg, and the seed the size of the egg of a pigeon. The seed is covered with a dense felt of blond coarse hair, weighs about 6 grams, and contains 54 to 66.8 per cent of tallow. The natives boil the seed in water and lift the cake of tallow after cooling. The recovered waxlike product is known as "dika butter."

The preparation of Cochin-China wax appears to be somewhat more extensive than that described for dika butter. The natives gather the fruit (nuts) in heaps, where they are left for two months or until the soft outer parts decompose, when they are carried to the houses and spread out in the sun to dry. They are then opened by a strong knife, and the kernels are removed, dried in the sun, and pounded in a mortar. The pulp is placed in a sort of crude doubleboiler, and on heating, a sticky paste is obtained. The paste, wrapped in rice straw, is submitted to pressure in a crude press, and the expressed wax is melted and cast into molds, or into candles in bamboo tubes provided with wicks. The dry kernel contains 52 to 60 per cent of wax, which is not fully recovered by the crude method of extraction. The press cake is used for fodder, fertilizer, or fuel. Five kilograms of nuts yield one kilogram of kernels and 430 grams of fat or wax. The wax is of a grayish color and may be refined by benzin extraction.

The analytical constants given in Table 59 for Cochin-China wax and dika butter are from two sources.

Native Cochin-China or cay-cay wax shows a much higher acid value than the one recorded above, probably because of the crude way in which it is handled and stored. Bontoux[34] gives the composition of the wax as *myristin* 60–65 per cent, *laurin* 30–35 per cent, and *olein* 5 per cent. It has been more recently shown that dika butters contain mixed glycerides, the chief component being *dilauromyristin*. Grimme[92] says that when the kernel of *I. gabonensis* is extracted with ether, it furnishes a tallow which is white, crystalline, and of agreeable odor; the yield is 67.8 per cent. According to Piraette[208] analyses of the tallow indicate that its composition is very constant, and the solid acids are chiefly *stearic* and *palmitic* with a small amount of *oleic* and volatile fatty acids.

The uses of Cochin-China wax are generally given as candlemaking and soap-stock material. When properly refined it is of value as an edible vege-

TABLE 59. ANALYTICAL CONSTANTS FOR COCHIN-CHINA WAX AND DIKA BUTTER

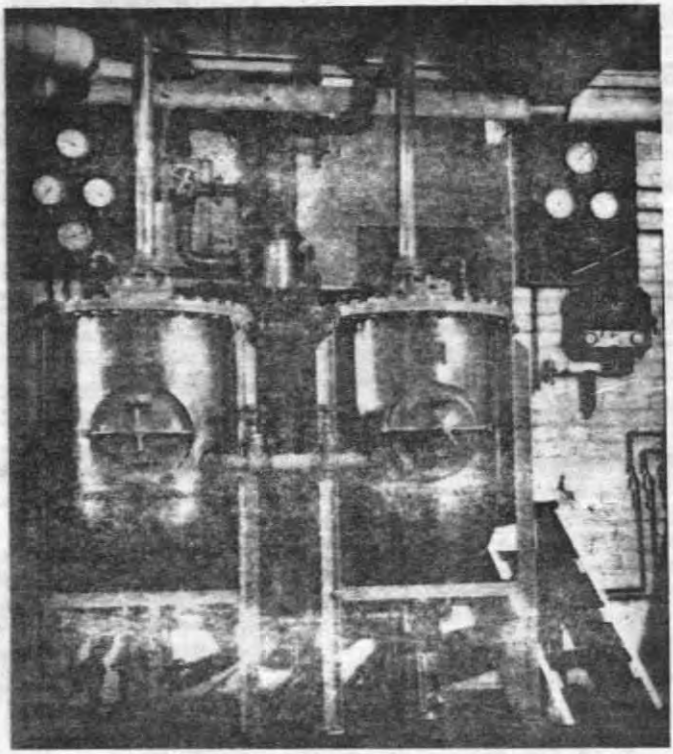
	Cochin-China Wax (Cambodia)	Dika Butter[27] (Sierra Leone)	Dika Butter[208] (Belgian Congo)
Wax or Tallow:			
Specific gravity	(d_{40}^{40}) 0.9130	(d_{50}^{50}) 0.9125	(d^{60}) 0.9043
Melting point	39.7°C (soft. 37°C)	39.9°C	37.5°C
Solidifying point	31°C	37°(?)C	36.2°C
Refractive index	—	(n_D^{50}) 1.4505	(n_D^{40}) 1.4488
Acid value	0.86	3.98	—
Saponification number	235.3	241.2	244.9
Iodine number (Wijs)	6.7	4.3	2.9
Fatty acids, per cent	93.58	94.38	—
Glycerol, per cent	—	12.96	—
Unsaponifiable matter	0.42	1.43	—
Polenske number	—	—	1.43
Reichert-Meissl value	0.62	—	0.70
Fatty Acids:			
Melting point	—	38.8°C	34.2°C
Solidifying point	36.6°C	38.1°C	29.0°C
Refractive index	—	(n_D^{50}) 1.4357	(n_D^{40}) 1.4368
Neutralization number	250.2	254.8	259.4
Iodine number	—	14.5	3.3
Mean molecular weight	224	218.3	216.2

table butter in chocolate making. Pieraerts[208] states that dika butter makes a better and more soluble soap than does coconut oil; it is useful in various pharmaceutical specialties; for cocoa butter substitute; and for the preparation of leather. Refined dika butter is an excellent culinary fat.

Cranberry Wax

Cranberry wax is the wax derived from the skins of the large or American cranberry, *Oxycoccos macrocarpus* Aiton (*Vaccinium macrocarpum* Ait.). It is natural to the outer skin of the berry where it serves as a water repellent. The wax coating is present to the extent of 0.15 of one per cent of the weight of the cranberry, together with a waxy water-insoluble substance, a hydroxy carboxylic acid of pentacyclic structure, known as *ursolic acid*. If petrolic ether is used as a solvent, in the cold, the wax may be extracted free from ursolic acid, but if dichloroethylene is used as the extracting solvent, ursolic acid is extracted as well as the wax. The wax cannot be appreciably removed from the skins by boiling water.

Cranberry wax of commercial quality has been economically prepared from cranberry waste by Nealy[198], at the plant of the Cranberry Canners, Inc., South Hanson, Massachusetts. The annual crop of cranberries is 500,000 to 800,000 barrels per year. From 1000 barrels of berries may be

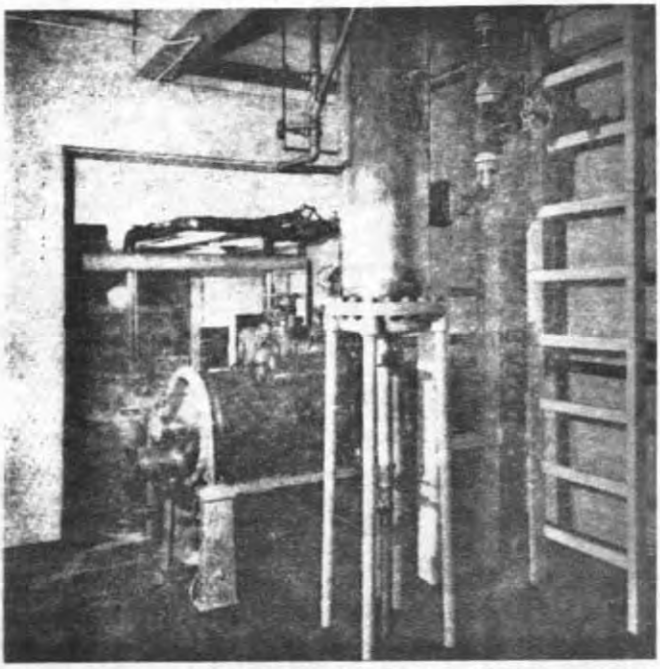


Courtesy Cranberry Packers, Inc., South Hanson, Mass.

FIGURE 8. Pilot plant for recovery of by-products of the cranberry.

obtained about 2000 pounds of washed and dried pulp consisting of skins, and 800 pounds of seeds. From the dried seeds mechanically separated from the pulp may be extracted 20–21 per cent of a greenish, semidrying oil, containing 200 units of vitamin A per gram; and from the dried skins about 12 per cent of a raw wax that the extractors refer to as *ursolene* and which is marketable in the pulverized condition, and in addition about 10 per cent of crude ursolic acid.

Carleton, Morris, and Nealy[45] describe the extraction process as follows: "twenty-five pounds of dried cranberry skins freed from seed are placed in a copper cylinder (presumably a still with water-cooled reflux condenser). Through this is passed the vapor of one of the extracting fluids for a period of time and at a definite temperature. It has been found that a 12-hour contact period is most effective for the extraction of either wax or acid from the skins. After one of the extracting solvents has been in contact with the skins for the desired length of time, the liquid flow is stopped and the second solvent permitted to contact the skins for an equal period of time.



Courtesy Cranberry Packers, Inc., South Hanson, Mass.

FIGURE 9. Recovery of solvents in extraction of ursoline wax and ursolic acid from cranberry waste.

The action of the solvents is specific in that cold hexane will extract the *wax* from the skins but will only remove mere traces of the *ursolic acid*. By utilizing the same skins and treating them subsequently with dichloroethylene practically all of the acid may be removed."

According to Nealy the character of the wax extracted from the skins is influenced by the temperature of the operation of the still, and also by the length of the time of extraction. After the extraction the solvent is recovered leaving the wax residue which can be separated as a layer. The product obtained from a low-temperature extraction with a considerable amount of water passing through the condenser is hence different from that of the high-temperature extraction. The latter hexane extraction yields a residue which has a tendency to stratify into layers in which the *nonacosane* constituent separates. The name *ursolene* is given to the product that represents everything extractable by hexane vapor at a temperature of 65–70°C (146–158°F). As it comes from the still it is pulverized to make it uniform in quality. The still has a thermoregulator control that makes it possible to lower the temperature of extraction by flowing more water through the condenser. By so doing most of the nonacosane is left behind and the

product is dark colored. The wax is softer and of lower melting point, but can be hardened by a heat processing in which certain of the unsaturated fatty acid constituents become oxidized.

Hence, several wax or waxy products can be commercially prepared, and these are summed up as follows:

(1) A soft, greenish wax by using hexane as a solvent with low temperature on thermoregulator. The wax melts at about 64°C, and is simply known as "cranberry skin wax."

(2) A hard, brownish wax by using hexane with a higher temperature. The wax contains a considerable amount of hydrocarbons—chiefly *nonacosane*, which are only properly dispersed by pulverizing the wax product of the still. It has a melting point of 207.5°C, and is called *ursolene*.

(3) A paler gray-green hard wax, obtained by using dichloroethylene as a solvent. This wax contains a considerable amount of hydrocarbons and of *ursolic acid*. It has a melting point of about 217.5°C and is termed "single extraction" wax.

(4) Heat-processed cranberry skin wax (1) in which an attempt has been made to oxidize the unsaturated fatty acids, and increase both the melting point and hardness. The product is blackish.

(5) Ursolic acid, a white-colored product, which is extracted from *ursolene* residue after removal of the hexane extractable by dichloroethylene. This is "crude ursolic acid." The acid can be refined to obtain the c.p. ursolic acid (m. 283°C, neutralization value 122.8).

In preparing ursolene the residue as removed from the still is first broken down into irregular lumps. It is seen to be nonhomogeneous, and varies from gray to green in color. Upon further pulverizing it is of greenish color. The so-called "single extraction wax" was first prepared by Nealy, and differs from the other waxes in containing a larger proportion of ursolic acid plus much *nonacosane* with a lesser proportion of the softer wax constituents. It is hard and brittle. The constants for the cranberry wax and waxy products are listed in Table 60.

Ursolic acid has a neutralization value of 122.8, and an iodine number of 55.6. The glycerides consist of about 20 per cent palmitin, 30 per cent linolein, and 50 per cent olein, or their equivalents in mixed glycerides; also a little linolein. The glycerides have a saponification number of 194, and an iodine number of 86. The free fatty acid (m. wt. 278.4, neut. value 201.5, iodine no. 109.7) is believed to consist principally of oleic acid. The free fatty acids constitute about 14 per cent of the proportional amount of the glycerides present in the wax. The composition of the cranberry waxes has been computed here on the basis of their chemical constants.

The heat processing of ursolene by blowing it with air causes a reduction in the glycerides from approximately 46 to 23 per cent, but an increase

TABLE 60. ANALYTICAL CONSTANTS FOR CRANBERRY WAX AND WAXY PRODUCTS

	Cold Extraction, Normal Hexane	Raw Cranberry Wax, Hot Hexane Extraction	Similar, Pulverized, Known as "Ursolene"	Single Extraction with Dichloroethylene	Hexane Extractive, Heat Processed with Blown Air	Ursolic Acid, Purified
Melting point (°C)	64	212.0	207.5	217.5	194.0	283.0
Specific gravity (d^{15})	0.970	0.975	0.975	0.970	1.010	0.970
Acid value	23.0	59.1	42.2	69.3	42.1	121.5
Saponification number	181.0	134.0	130.0	131.0	85.0	123.5
Ester value	158.0	74.9	87.8	61.7	42.1	2.0
Iodine number (Hanus)	69.0	52.2	53.2	44.2	57.4	55.7
Hardness (Shore at 25°C)	75	100	100	100	100	100
Ursolic acid (%) (estd.)	tr	39.2	24.0	49.2	24.4	98.9
Hydrocarbons (%) (estd.)	7.2	15.9	23.5	13.8	23.9	none

TABLE 61. APPROXIMATE COMPOSITION OF CRANBERRY WAXES

	Soft Wax (m. 64°C) (cold petrolic ether extract) (%)	Ursolene (m. 207.5°C) (hot normal hexane extract) (%)	Single-Extraction Wax (m. 217.3°C) (dichloroethylene) (%)
Mixed Glycerides of:	81.4	46.2	32.5
C_{18} unsaturated acids			
C_{16} saturated acid			
Free Fatty Acids	11.4	6.3	4.5
C_{18} unsaturated acids			
C_{20} saturated acid			
Free Polycyclic Acids	mere trace	24.0	48.0
Ursolic acid (α-m. 283°C)			
Hydrocarbons	7.2	23.5	14.1
Nonacosane			
Hentriacontane			

in the free fatty acids from about 6 to 30 per cent, while the ursolic acid and hydrocarbons remain substantially unchanged.

The chemical composition of cranberry wax extracted from crude cranberry waste pulp by petrolic ether has been given by Markley and Sando[176]. It was found to contain glycerides of linolenic, linoleic, and considerable oleic acid, besides a very large amount of unsaponifiables consisting of the hydrocarbons, nonacosane, and hentriacontane. The solid fatty acids were of the usual mixture of plant acids of the series C_{16} to C_{26}. In the distillation they separated seven fractions with 52.3–80.0°C melting point, and the neutralization values ranged from 142 to 208. The four main fractions of

hydrocarbons showed a melting point of 63.2–64.5°C, and the chemical composition C_{29} and $C_{31}H_{64}$.

The cranberry dry pulp after extraction with hexane to recover the wax is treated with ethylene dichloride which extracts a waxy acid of considerable value, namely *ursolic acid*. Ursolic acid was first found in uva ursi leaves, but later in the skins of the apple and pear, and in considerable quantities in the skin of the cranberry. According to Nealy it is estimated that from twenty to thirty thousand pounds of ursolic acid a year can be recovered from cranberry waste now available for that purpose.

Ursolic Acid. Ursolic acid, which is a sapogenic acid, has the formula $C_{29}H_{46}(OH)COOH$ with a molecular weight of 456.68. Refined ursolic acid is a very fine and fluffy white powder (231 cu in. to 1 lb). It is refined through its monosodium salt from the impure form. It has neither taste nor odor, is nontoxic, and is insoluble in water, hot or cold. It is insoluble in aqueous solutions of alkalies. It is soluble in alcohol, and in benzene. One per cent of ursolic acid in ammonia will produce a thick colloidal solution. Ursolic acid has appeared in the chemical literature under the name of urson, prunol, malol, etc. It is a major constituent of the skin of the cranberry, *Vaccinium macrocarpum*. It is found in the leaves and berries of the bearberry, *Arctostaphlos uva-ursi*; in *Rhododendron hymenanthes*; and in the waxlike coatings of apples, pears, prunes, and other fruits.

In the refined state ursolic acid as crystallized from 75 per cent alcohol melts sharply at 283–283.2°C, but it is not stable to heating at a high temperature. There are now known to be two acids, β-ursolic acid, obtainable from rhododendron leaves, which melts at 290–291°C; and *α-ursolic acid* which melts at 281–283°C. The latter is close to oleanolic acid in its chemical structure, the double bond being at the 13:18 position, instead of the 12:13 position, and both have the COOH in position 23. On the other hand, *α-ursolic acid* has the double bond in the 12:13 position with the COOH in position 5[111a].

Ursolic acid when added in small quantity to paraffin wax will like carnauba boost its melting point. Since ursolic acid has an OH group it is capable with acetic anhydride of forming an acetate (m. wt. 498.72, saponification number 225, iodine number 50.9, neutral. number 112.5). The same constants apply to oleanolic acid; the acid component constitutes 91.4 per cent of the ester.

Uses of Cranberry Waxes. Few, if any, uses have been developed for cranberry waxes, due to the fact that upon melting they tend to stratify into layers of diverse physical properties, the hydrocarbons separating from the glycerides, etc. Ursolic acid is probably the most valuable constituent. According to Nealy[198] ursolic acid is an excellent emulsifying agent. It will produce what is known as a reverse emulsion, that is a water-in-oil emul-

sion instead of the usual oil-in-water type, the droplets of water being suspended in the oil instead of the oil being suspended in the water. As small an amount as 3 parts of ursolic acid to 1000 parts of the ingredients will produce a smooth, firm emulsion that will stand up without any support. It is said to be of value in preparing salad dressings.

A cream called "Vaccinol" has been prepared from cranberry seed oil, ursolic acid, and distilled water, and has proved of value in the treatment of burns. It removes the soreness almost immediately and the burn heals in a very short time. "Vaccinol" has also been very successfully used in skin disorders such as eczema.

Apple Skin Wax

The apple, *Pirus malus* L., family order Pomaceæ, and its related species contain a wax on the cuticle of the fruit. The wax is also referred to as apple cuticle wax. Sando[240] has reported on the wax from the skins of Ben Davis, and Black Ben Davis varieties, and the numerous constituents that naturally occur in apple cuticle wax. One pound of wax is obtained from 43 square yards of peel from one type of apple to 231 square yards from another type. 140–175 mg of wax can be obtained from 100 grams of "fresh tissue" by extraction with alcohol and ether. Riviére and Pichard[231a] dried the apple skins at 50 under a current of dry CO_2, and then extracted them with carbon tetrachloride to remove the waxy materials; the residue after evaporation of solvent wax analysed for its chemical constituents. In its crude state apple cuticle wax is a greenish-yellow powder, resinous to the touch, and very repellent to water. It has a melting point of approximately 80°C.

Apple cuticle wax was found to be chemically composed of paraffin hydrocarbons, ketones, primary alcohols, and secondary alcohols by Chibnall and associates[48]. Sando[240] in 1923 isolated *triacontane* ($C_{30}H_{62}$ m. 63.5–64°C), subsequently confirmed by Riviere and Pichard[231a]. In 1931 Chibnall and Piper identified *nonacosane* and *heptacosane* as constituents. They also identified *hexacosanol*, *octacosanol*, *d-nonacosan-10-ol*, and *triacontanol* as components. Riviére and Pichard[231a] reported the presence of *heptacosanol* ($C_{27}H_{55}OH$, m. 81°C). It is now believed that apple cuticle wax contains C_{26} and C_{28} alcohols, namely *hexacosanol* and *octacosanol*, *d*-10 *methyloctacosanol* ($C_{29}H_{59}OH$), but no heptacosanol, and the C_{27}, C_{29} and C_{30} hydrocarbons referred to above.

In 1923 Sando[240] isolated a cyclic hydroxy acid which was called *malol* ($C_{30}H_{48}O_3$, m. 284–285°C). Malol forms a crystalline monosodium salt and is dextro-rotatory. Malol contains a carboxyl group, and conforms to the generic formula $C_{29}H_{46}(OH)\cdot COOH$, comprising at least five benzene rings and a number of methyl groups. Malol is now considered as identical to *α-ursolic acid* (m. 283°C), and consequently the name *malol* has been

dropped. Ursolic acid in the purified state as crystallized out from 75 per cent alcohol is a pure white crystalline powder, the crystals being prismatic in shape. Ursolic acid is insoluble in petroleum benzin, soluble in glacial acetic acid or alcohol, and moderately soluble in ether, acetone, and chloroform. Fresh apple leaves also yield ursolic acid, to the extent of one per cent.

Wax of Pear Cuticle

A wax can be separated from the peels of the common pear, *Pyrus communis* L., obtained in commercial canning. According to Markley, Hendricks, and Sando[177], the fruit coat wax is light green in color and of low melting point. The separation of the lipid wax is effected with petrolic ether, and 40 per cent of the extract consists of free and combined acids, about half being in the unsterified state. The solid acids appear to be of the series C_{16} to C_{24}. The predominant acid is oleic, accompanied by very small amounts of linolenic and linoleic acids, which can be isolated from the liquid fraction. There is a small amount of glycerol but no secondary alcohols or ketones. The solid fraction contains ternary mixtures of primary alcohols of the series C_{20} to C_{30}. Both *lignoceryl* and *ceryl alcohols* predominate. *Nonacosane* (m. 65.1°C) is the predominant hydrocarbon, and *ursolic acid* is a constituent. The latter had been previously extracted by Seifert in an impure form (m. 240°C). The alcohol *d-noncosan-10-ol* found in apple cuticle wax could not be definitely recognized in the wax of the pear cuticle.

Wax of Pineapple Cuticle

The cuticle of the pineapple, *Ananas comosus* (L.) Merr. contains a lipid wax. Feurt and Fox [78a] extracted 1.4 per cent of soft wax from the waste of pineapple fruits by means of organic solvents such as acetone, chloroform, and petrolic ether. They report the following analytical constants for pineapple wax: saponification number 232.4, acid value 57.1, ester value 175.3, iodine number 49.9, and unsaponifiable 59.5 per cent. The wax is soft in consistency, and melts at 51°C. They found it contains an appreciable amount of steroids.

Prunus Waxes

The wax in the skins of various species of *Prunus*, family order Drupaceæ, such as the mazzard cherry, *Prunus avium* L.; the apricot, *P. armeniaca* L.; and the common prune, *P. domestica* L.; is much the same in character as that of many varieties of apples. The principal constituent of the prune, previous to the researches of Van der Haar[95] in 1925, was called prunol, which proved to be the same as *ursolic acid* found in the skins of other fruits.

The skins of the Bing variety of mazzard cherries, *P. avium*, have been

examined with respect to the constituents soluble in petrolic ether and ethyl ether, by Markley and Sando[178]. From the petrolic ether extract have been isolated or identified solid fatty acids consisting of a ternary mixture of *palmitic*, *stearic*, and a small amount of *arachidic acid* (?); liquid fatty acids, *linoleic* and *oleic*; a small amount of glycerol; and the hydrocarbons *nonacosane* and a higher one. The ether extract yielded *d-glucosidylsitosterol* and *ursolic acid*. The dried skins yield 0.8 per cent petrolic ether extractives, and 0.1 per cent ethyl ether extractives.

Power and Moore[214] extracted 12.6 kg of air-dried leaves of black cherry, *P. serotina* Erhr., commonly called chokecherry, with hot alcohol; the excess alcohol was removed by evaporation, and the resultant extractive was submitted to steam distillation. The distillate yielded a volatile oil, and the residue in the distillation flask consisted of a dark green aqueous liquid and a green resin, which was found to consist of *hentriacontane*, $C_{31}H_{64}$; *pentatriacontane*, $C_{35}H_{72}$; *ceryl alcohol*; *palmitic*, *stearic*, *linoleic* and *isolinoleic acids*; *ipuranol*, $C_{23}H_{38}O_2(OH)_2$; and *prunol* (ursolic acid, m. 275–276°C).

The ethyl ether extract of the pulp of the fruit of Japanese apricot, *P. mume*, contains *sitosterol*, *ceryl alcohol*, *hentriacontane*, and *oleanolic acid*, $C_{30}H_{48}O_3 \cdot H_2O$ (m. 295–296°C), the structure of which is given on p. 32.

Grape Pomace Wax

In 1938 Markley and his collaborators[178a] reported that they had exhaustively extracted the air-dried pomace of the Concord grape (Northern fox grape), *Vitis labrusca* L., with petrolic ether and then with ethyl ether, and had obtained 4.0 and 3.4 per cent of extractives respectively. The petrolic ether extract after saponification upon analysis revealed glycerol; linoleic, oleic, palmitic, stearic, and higher members of the saturated series C_{20} to C_{32} acids; the hydrocarbons *nonacosane* and *hentriacontane*; *sitosterol*; and fractions representing mixtures of primary alcohols of the saturated series C_{22} to C_{28}. The ethyl ether extract consisted principally of *oleanolic acid*, $C_{30}H_{48}O_3$, together with unidentified resinous substances. Like ursolic acid found in the skin of the cranberry, and cuticle waxes of the apple and pear, oleanolic acid is a polyterpene sapogenin containing a pentacyclic nucleus of five condensed benzene rings. It belongs to the β-amyrin group, whereas *ursolic acid* belongs to the α-amyrin group, of triterpenes. Oleanolic acid is also found in the sugar beet, on the clove bud, and in olive leaves.

The most valued constituents of the waxes on the various fruit skins are the sapogenins, which can be freed from the saponifiable matter by treatment with dilute sodium hydroxide, acidifying and crystallizing the sapogenin from a 75 per cent alcohol solution. The sapogenins are valued as

emulsifying agents. They are not toxic and can be used for coating any delicate objects that need to be moisture proofed, such as nuts, cookies, candies, etc. They will probably prove to be of considerable value to the cosmetic industry as well.

Ucuhuba Wax

Ucuhuba wax, a tallow derived from the kernels of the nut (seed) of the ucuhuba (ucuúba), *Myristica surinamensis* Blume (*Virola surinamensis* Warburg), the fruit of a white species of evergreen tree, is indigenous to the lower region of the Amazon River, Brazil. The seed is spherical, weighs 1.3 grams, and has a thin, easily removable shell revealing a kernel covered with extraordinarily large and handsome albuminous crystalloids. The kernel contains 65 to 76 per cent of glycerides and 6 to 7 per cent of undesirable dark-colored resinous matter. A closely related species, *Virola sebifera* Aublet (*M. sebifera* Swartz) is indigenous to the same region. This red species is the source of *Ocuba wax*, or *Virola tallow*, but is also marketed as Ucuhuba fat or tallow. The genus *Virola*, order Myristicaceæ, includes several species found in the Guianas, Panama, Guatemala, and Venezuela, such as the evergreens *V. guatemalensis* Warburg and *V. venezuelensis* Aublet. The crude tallow is customarily freed from crushed nuts by boiling them in water. The tallow as marketed is a dark yellow grease with a slight ethereal odor. It also has been produced by pressing the seed with oil rolls, or by extracting the crushed seed with a solvent such as hexane. The latter method produces a tallow of lower resin content.

Virola bicuhyba (*M. bicuhyba* Schott) of southern Brazil yields black wrinkled seeds which are a source of *bicuhiba tallow*. *Myristica platyferma*, of Brazil, is the source of a *bicuhyla tallow*. The nut yields 59.3 per cent of oil or tallow, the kernel 32.6 per cent. *M. fragrans* Houtt., of Molucca Islands, is the source of nutmegs (U.S.P.) and mace; *M. otoba* Humb. & Bonp, of Colombia, the source of Otoba butter; the arriloid of the nut is white mace; *M. angolensis* (*Pycnanthus kombo*), of West Africa, the source of Kombo butter; and *M. scyphocephalium* (*S. ochocoa*), of Colombia, the source of Ochoco butter.

Ucuhuba wax as marketed is considered to have the following physical and chemical constants: melting point 41–44°C; density (d^{15}) in solid form 0.9950, density (d^{78}) in liquid form 0.8882–0.8855; refractive index (n_D^{70}) 1.4431–1.4445 (Zeiss n_{10} 50.1–61.6); acid value 8.4–20.7; saponification number 215–229; iodine number (Wijs) 10.9–14.1; Hehner number 93.4; R-M value 1.5–1.6; Polenski number 3.9–4.0; and unsaponifiable 0.9–2.5 per cent.

Steger and van Loon[269] extracted the seed of *V. surinamensis* with petroleum ether and obtained 65.1 per cent of ucuhuba tallow which was

TABLE 62. CHARACTERISTICS OF TALLOWS OBTAINED FROM SPECIES OF *Myristica* AND RELATED GENUS *Virola* (*Myristicaceae*)

Name	Index n_D Refraction	Melting Point (°C)	Specific Gravity	Sapon. Number	Iodine Number
V. surinamensis (Ucuhuba tallow)	1.4446 @ 70°C	51	0.8882 @ 78/4°C	224	10.9
V. sebifera (Virola tallow)	—	45–50 (40° s.p.)	0.920 @ 15°C	—	—
V. guatemalensis[93] (Noix de dragonier)	1.4539 @ 50°C	41 (38.5° s.p.)	0.9005 @ 50°C	223–244	13.8
V. venezuelensis[92] (Cuojo butter)	1.4541 @ 40°C	47 (44.5° s.p.)	0.8996 @ 50°C	221	12.4
V. otoba[21] (Otoba butter)	1.4710 @ 40°C	34	0.9293 @ 20/20°C	185	54 (Hanus)
M. platyferma[23] (Bicuhyla tallow)	1.4502 @ 40°C	41–43	—	240	5–6
M. scyphocephalium[156] (Ochoco butter)	1.4496 @ 40°C	45–48	0.8899 @ 60/4°C	238.5	1.7
M. canarica (Mangalore butter)	1.4648 @ 40°C	37–39 (titer 34°C)	—	203–215	19–27
M. angolensis (Kombo butter)	—	40 (titer 37°C)	0.8870 @ 99/15°C	255	65.4
M. malabarica (Malabar butter)	1.4584 @ 40°C	31–32	—	189–192	50.4–53
M. bicuhyba (Bikuhiba tallow)	1.4583 @ 40°C	40–47	—	218–228	10.5–18
M. fragrans (Nutmeg butter)	1.4683 @ 40°C	42–52	0.8840 @ 100°C	160–180	45–49

light in color, and had the following characteristics: melting point 51°C, refractive index (n_D^{70}) 1.4446, acid value 8.4, saponification number 223.9, R-M value 1.6, Polenski number 9.7, unsaponifiable 2.2 per cent. The fat acids had an iodine number 9.7, refractive index (n_D^{70}) 1.4322, melting point 48°C, saponification number 236, and average molecular weight 238. The fat acids consist of *lauric* 12.6, *myristic* 63.2, *palmitic* 8.4, *stearic* 1.5, *oleic* 6.3, *linoleic acid* 2.8, and resinous matter 5.2 per cent. *Virola* species carry more lauric acid than do *Myristica* species.

The chemical composition of the fatty acids obtained by the hydrolysis of the glycerides of various grades of ucuhuba wax has been reported as follows: *lauric* 5.0–13.3, *myristic* 66.6–73.0, *palmitic* 8.9–11.0, *stearic* 1.5, *oleic* 6.5–11.0, *linoleic* 3.0 per cent.

Chemical Composition of Ucuhuba Wax. Ucuhuba wax is composed of 43 per cent of *trimyristin*, mixed glycerides and resin. The mixed glycerides comprise *laurodimyristin* 31 per cent, *oleolauromyristin* 12 per cent, *lauromyristopalmitin* 10 per cent, *oleodimyristin* 3 per cent, and *dilauromyristin* 1 per cent. The resin gives a fuchsin-red coloration on the addition of a drop of concentrated sulfuric acid, is insoluble in petrolic ether, melts at above 100°C, and has an acid value of 105.5, saponification number 195.3, and unsaponifiable 3.9 per cent. Ramos and Nascimento[223] report having isolated 1.26 per cent phytosterol from ucuhuba wax.

Preparation of Myristic Acid from Myristica Tallows. Pure *myristin* and pure *myristic acid* are best prepared from the so-called butter of the nutmeg, *M. fragrans*, although a good grade of myristic acid is obtainable from ucuhuba tallow. Verkade and Cooper[303] described the following method: Nutmeg butter (340 g) is crystallized from 2000 ml of a mixture of 4 volumes 96% ethanol and one volume ether and the crude trimyristin (326 g) is melted up with bone charcoal, filtered and again crystallized from 2500 ml of the solvent mixture giving 312 g of pure trimyristin (m. 55°C). Trimyristin (100 g) is melted in a large porcelain dish; 80 ml ethanol and 80 ml of 35% aqueous NaOH are added and the mixture is warmed on the steam bath until the alcohol has evaporated; again 80 ml ethanol is added and evaporated off in the same way. Two liters of boiling water is now added and subsequently when all of the sodium soap has dissolved, 500 ml of 10% sulfuric acid. The mixture is now heated on the steam bath until the myristic acid has separated completely on the surface of the aqueous layer; it is allowed to cool and the cake of myristic acid is again melted with 2 liters of water. The acid so obtained in almost quantitative yield solidifies at 51.1°C and on a single crystallization from 80% ethanol, 80% acetone or ether, yields myristic acid with the correct setting point 53.6°C.

To recover myristic acid from ucuhuba tallow the tallow (500 g) is dissolved in 5 liters of petrolic ether (b. 40–60°C) and the whole allowed to

stand for several hours; a dark-colored resinous matter then has collected in the bottom of the flask. The solution is filtered, the solvent evaporated, the tallow saponified in the way described above, and the free acids distilled *in vacuo*, the portion distilling below 215°C at 12 mm being collected (365 g). A purer product (setting pt. 52.3°C) may be obtained through fractionation of its methyl esters.

Uses of Ucuhuba Wax. Tallows derived from the various species of *Virola* and *Myristica* do not fall in the edible class, because of the resinous matter which they contain, and which is considered toxic and makes them unpalatable. The word *myristica* is derived from the Greek meaning "fit for annointing." Natives have used the tallows in religious services, as ointments with medicinal properties, and in candle making. Ucuhuba tallows have been exported from the tropical countries to the United States and to Europe for soapmaking.

Crude ucuhuba tallow can be freed from the objectionable resin by extracting the glycerides with a light petroleum spirit in which the resin itself is insoluble, whence the solvent is recovered by distillation, and the fat residue bleached by treatment with activated carbon. The fatty acids can be recovered by Twitchellizing the tallow and distilling the resultant fatty acid. The latter can then be separated by the *Emersol process*, a method of solvent fractionation, which is continuous and employs methanol as a solvent and as a heat interchange medium in the multitubular crystallizer. Filterable crystals of the solid acids may be expedited by the addition of a crystal promoter to the methanol solution.

Although the brown color of ucuhuba wax, or tallow, has to some extent interfered with its general use commercially, it is said that in 1941 over 2,000,000 pounds were exported to the United States ostensibly for the manufacture of high-grade vegetable soap.

Murumurú Wax

Murumurú wax is not a true wax but a vegetable tallow derived from the murumurú astrocaryum, *Astrocaryum murumurú* Mart., of the order Sabalaceæ, a thorny palm of the tribe *Coryphineæ*. The palm is indigenous to tropical America, and flourishes in the State of Para, Brazil. According to Knaggs[128], the fruit, which contains the wax-bearing seeds, is pear-shaped and covered with small spines: it is brown in color and turns yellow when ripe.

The wax is an unctuous material, which because of its relative softness is often referred to as murumurú butter. It has the following characteristics: density (d^{15}) 0.9180, saponification number 238–242, iodine number 5.45–12.4, neutralization value 2.69–18.0, melting point 33–35.8°C, refractive index (n_D^{15}) 1.4535. Murumurú contains *glycerides* of *lauric*, *myristic*, and *palmitic acids*, as well as other components.

During World War II considerable quantities of the wax were imported for use in the manufacture of soaps, the murumurú being used in place of coconut, palm kernel, and other vegetable oils not freely obtainable at that time. At the beginning of exportation of murumurú to the United States, most of the product was shipped in the form of seed for expressing. Later, the Brazilian exporters developed equipment to do their own expressing. Murumurú butter or fatty acids derived from partially saponified stock are condensed by heat with methylmonoamine, and the condensation product is then sulfonated or phosphated to produce surface-active agents useful as detergent and emulsifying agents in bleaching and dyeing processes[297a]. In 1943 Brazil exported nearly one million pounds of the expressed wax, and a half million pounds of seed.

Gueriniella Wax

A waxy substance from a plant, *Gueriniella serratula* Fabricius, has been studied for its chemical and physical characteristics by Prandi[217]. The crude wax is reddish yellow, and of a disagreeable rancid odor. It can be separated into 23.8 per cent of an ether-soluble tallow-like substance, and an ether-insoluble waxy substance. The tallow had a melting point of 54–56°C, setting point 49–51°C, and density (d_{15}^{15}) 0.874, and contained 26.5 per cent of free fatty acid. The ether-insoluble wax when recrystallized from benzene formed minute white scales of silky luster and unctuous feel. The constants given for the wax are as follows: melting point 88–89°C; solidifying point 88°C; density (d_{15}^{15}) 0.985; refractometric degree (Zeiss butyro-refractometer) reduced to 40°C, 48.7; saponification number 69; acid value 0; ester value 69; Hehner number 53.3. The wax is very soluble in hot benzene, chloroform, and carbon disulfide; quite soluble in cold chloroform and in carbon disulfide; and slightly soluble in cold benzene.

The chemical composition of gueriniella wax appears to comprise esters of the higher monohydric alcohols, C_{28}, C_{28}, and C_{30}, with somewhat lower monocarboxylic acids. *Myricyl triacontanoate* (m. 92.5°C) is believed to be the chief component. It contains no unsaturated compounds and no phytosterols.

Opium Wax

Opium wax is a constituent of the concrete exudation from unripe capsules taken from the opium poppy, *Papaver somniferum* L., indigenous to the Mediterranean region, but largely cultivated in India. This species of poppy is the source of opium and morphine. The wax is only contained in the pericarp of the seed. About 7 per cent of the wax, which is brown and sticky, can be extracted from dry powdered opium by means of petrolic ether. The wax can also be obtained as a by-product in the preparation of morphine. Morphine is ordinarily extracted from opium by the André Bar-

bier process in which the solvent is water; the total alkaloids are precipitated from a concentrated solution of the extract by neutralizing it with sodium carbonate. The total alkaloids are then extracted with an organic solvent ($CHCl_3$) which removes secondary alkaloids, and leaves crude morphine in the insoluble residue. In the first step of the process in which the alkaloids are leached out with water, the nonalkaloidal residue left behind can be dried and extracted with chloroform to obtain the wax.

Opium wax is insoluble in water, almost insoluble in methanol or ethanol, and soluble with difficulty in acetone; but freely soluble in chloroform, carbon tetrachloride, ether, benzene, etc. The wax contains 28.7 per cent of unsaponifiable matter with an iodine number 138.5. The wax shows a very high iodine number 152.5, a Reichert number of 2, and a saponification number of 114.5, according to Rakshit[222]. The melting point is not well defined but somewhat above 40°C.

Opium wax in its crude state contains *palmitic acid*, *stearic acid*, and *linoleic acid*. The latter is the principal constituent of the glycerides in the seed oil. The unsaponifiable matter contains *sitosterol* and *ceryl alcohol*. Likely components are *ceryl palmitate* and *sitoserolin*. There is little difference in the iodine numbers whether determined by the Kaufmann, Hanus, Winkler, or Winkler-Awe methods. It is doubtful whether the wax would be of economic value.

Wax of Jambul Fruit

The pericarp of the esculent fruit, Java plum, or jambolan, *Eugenia jambolana* Lamarck (*Syzygium cumini*), or other jambul fruit has both lipid wax and resin components. Murti and Rao[196] extracted 2 kg of the dried pericarp with 4 liters of a 2.5 per cent HCl solution in methanol at room temperature for 2 weeks. The solution was heated with 10 liters of ethyl ether to precipitate the coloring matter. The solvents were then distilled off, and the volume brought up with 600 ml water. The pasty resinous products were extracted repeatedly with ether, and the brown residue was taken up in alcohol and recrystallized, giving a colorless compound (m. 232°C). The residue from the methanol-HCl extraction gave a little more of the same product, which upon saponification yielded an essential oil, a sterol (m. 135°C, acetate m. 121°C), and potassium oleanolate.

Wax of Perubalsam Balm

The fruit of the Perubalsam balm tree, *Myroxylon pereirae* (Royle) Klotzch, family Leguminosae, contains a wax. The tree exudes from its trunk a viscid balm known as "Balsam of Peru," much used in medicine. The fruit is a yellowish-brown legume. The tree is native to the mountainous regions of Central America, especially El Salvador. A substance called

white balsam is procured from the fruit, in Mexico. This balsam contains 67.7 per cent oleroresin, 14.8 per cent wax, 11.9 per cent acid resin, with small amounts of tannin, glucose, moisture, etc. The pericarp of the fruit contains 0.83 per cent wax. [*Chem. Abstracts*, **12**, 1329 (1927)]. Little is known of the composition of the wax, which appears to be of academic interest only.

Waxes in Citrus Peels

The rinds of the sweet orange, *Citrus sinensis;* sour Seville orange, *C. aurantium* Risso; Bergamot orange, *C. bergamia*, Risso et Poit, source of the oil of bergamot; Coorg or loose-jacket orange, *C. nobilis* of India; lemon, *C. limonia* Risso; bitter orange, *C. vulgaris* Risso, the flowers of which are the source of the oil of Neroli; the lime, *C. aurantifolia* (*C. limetta* Risso); and the grapefruit, *C. paradisi;* all yield a very small amount of wax. The citrus waxes comprise both crystalline and noncrystalline types; they are soft, somewhat colored, and of relatively low melting points. They are extractable from fruit rinds; some of the wax constituents may be found in the pulp as well as the peel.

The nonvolatile residue which remains after the distillation of the citrus fruit peels is most often quite waxy, and the wax may be extracted from it by chloroform. Wax also settles out from the essential oil obtained in the pressing process of citrus peels, since some of the wax originating in the peel becomes dispersed in the oil but settles in the course of time. For example, 0.37 per cent of crystalline wax has been obtained from oil of lemon, 0.21 per cent of wax from the loose-jacket orange, and 0.56 per cent of wax from the Sylhet orange, *C. indica.* The wax may be removed from the oil by filtration, and freed from traces of oil by steam distillation. Dutt and Prakash[72a] (Univ. Delhi, India) report that sweet orange (*C. sinensis*) contains 0.29 per cent of crystalline and 0.68 per cent of noncrystalline wax. Seville orange (*C. vulgaris*) oil contains 0.13 of crystalline and 1.9 per cent of noncrystalline wax.

The wax of the cold-pressed oil of the Spanish orange (*C. vulgaris*) has been separated by Gonzales-Trigo[89] from the essential oil by the last described method. It is reddish in color, somewhat unctuous, of not a well-defined odor, and possesses a slightly bitter taste. The wax is very soluble in ether and chloroform, and partially soluble in most organic solvents; it is insoluble in water. The wax has a specific gravity (d^{15}) of 0.9853, melts at 44–46.5°C, solidifies at 36–38.5°C, and has a refractive index (n_D^{20}) of 1.5023; it is optically inactive; it is translucent in fine layers and transparent when melted. The chemical constants are: acid value 48.31, saponification number 120.93, ester value 72.62, Hubl's index 2.50, Buchners index 38.64, iodine number (Hanus) 115.72; Hehner's index 93.20, hydroxyl index

(André) 52.41. The bitter taste of the wax is probably caused by hesperidine.

The nonvolatile residue of São Paulo (Brazil) orange oil was clarified by Iaachan and Gottlieb[112] by filtering its 5 per cent solution in chloroform through a mixture of activated carbon and kieselguhr. The resulting odorless product was a wax, which had the following analytical constants: melting point 37–40°C, specific gravity (d^{25}) 0.9706, refractive index (n_D^{20}) 1.4903, acid value 2, saponification number 90. The authors suggested its utilization as a substitute for lanolin in many uses, as a partial substitute for beeswax in polishes, and as a plasticizer in varnishes.

Gonzales-Trigo[89] report that the wax of the Spanish orange (*C. vulgaris*) upon saponification yields insoluble fatty acids with the following constants: melting point 31.5–32°C, solidification point 23.5°C, iodine number (Hanus) 36.12, neutralization equivalent 175.65, average molecular weight 319.38. Fractionation of the lead salts showed the presence of *palmitic, stearic, cerotic,* and probably *oleic, linoleic,* and *linolenic acids*. The unsaponifiable part (37.24 %) melted at 79–80°C and had an iodine number (Hanus) of 150.84. It contained 30.86 per cent of solid *hydrocarbons*, 30.24 per cent of coloring matter, and 38.90 per cent *sterols*. Fractional crystallization of the latter gave five sterols: $C_{26}H_{48}O_2$ or $C_{27}H_{48}O_2$, white brilliant scales (m. 150°C, acetate $C_{31}H_{52}O_4$ m. 114.5°C); $C_{26}H_{46}O_2$ (m. 139.5°C, acerate m. 97°C); and three other sterols melting at 141–142°, 133–134°, and 110–115°C respectively. The aforesaid acids had been previously found in the Valencia orange, *Citrus aurantium sinensis* L. *Lignoceric acid* is also a probable constituent. In fact, acids in the C_{16} to C_{28} range are common to citrus fruit peels. The pulp of the orange contains the hydrocarbon *pentacosane*, which is not present in the peel. The peel contains higher hydrocarbons. Ordinary *sitosterol*, $C_{27}H_{45}(OH)\cdot H_2O$ (m. 142°C), has been reported as a constituent but not the *hydroxy sterols* of the $C_nH_{2n-8}(OH)_2$ type of Gonzales-Trigo. The unsaturated acids are in the form of glycerides.

These substances have their origin in the cuticle of the fruit; they are dissolved by the oil in the pressing process. The quantity of cuticle wax, also referred to as sapogenic wax, obtainable from citrus fruits in general is so small as not to evoke much interest in its commercial recovery from fruit-cannery or essential oil industry wastes. The waxes if recovered might however find use in the food industry.

Wax of Grapefruit. The cuticle of grapefruit contains a wax. Grapefruit peel wax is recoverable from the oil of grapefruit prepared from the peel, after the peel oil has been subjected to a low enough temperature for the crude wax to settle out as a residue in storage.

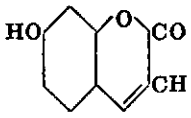
In the canning industry the grapefruit is mechanically halved, and the content of fruit removed, or passed through a juice extractor. A very thin

layer of the outside peel is shaved from the grapefruit refuse which is then ground into small particles. The essential oil is removed from the peel particles by a continuous flow of water, employing the countercurrent system. The recirculation of water over the peel particles washes out the oil by forming an emulsion. The emulsion is broken by centrifuging twice in a Sharples centrifuge (operating at 500 rpm). The yield of the clear amber-colored grapefruit peel oil is about one pound for each ton of grapefruit.

When the grapefruit oil is permitted to stand in storage (in stainless steel vessel) at a temperature of about $-10°C$, a wax of a light tan color and a pronounced taste and odor which is not disagreeable settles out. The crude wax constitutes 7 to 10.5 per cent of the weight of the oil. The wax because of its crystalline nature may be readily filtered from the oil, but to be useful must be freed from residual oil by vacuum distillation. Further refinement requires the use of selective organic solvents; the yield of refined wax is less than 3 per cent.

In 1937 Markley and his co-workers[178b] found that the nonvolatile waxy residue from Florida grapefruit, *Citrus paradisi* L., remaining after distillation of the oil contained a solid fatty acid of a mean molecular weight equivalent to $C_{32}H_{64}O_2$, as well as *linolenic*, *linoleic*, and *oleic acids*. They also isolated a sapogenic ketone, $C_{30}H_{52}CO$; hydrocarbons, $C_{29}H_{60}$ (*nonacosane*) and $C_{31}H_{64}$ (*hentriacontane*); a phytosterol, $C_{28}H_{42}OH$, which is probably *sitosterol*; and a new compound, *umbellifferone*, $C_9H_6O_2$. In 1949 Dutt and Prakash[72a] reported that grapefruit oil contains: *d*-limonene 92.72 per cent, methyl anthranilate linaloöl 0.9 per cent, crystalline wax 0.53 per cent, noncrystalline wax 2.05 per cent, crystalline coumarone derivative (m. 231°C) 1.06 per cent, loss and unidentified 2.1 per cent.

Hugh[110b] has attempted to isolate and identify some of the waxlike constituents in the peel oil of Arizona grapefruit (*C. grandis*, var. Marsh seedless). Hugh employed acid hydrolysis in the procedure and as a result separated the following: (a) A pale yellow oil [n_D^{20} 1.4274, dinitrophenyl hydrazone deriv. m. 103.5–105°C]. (b) A yellowish crystalline solid [m. 231–232°C, acetyl deriv. long silky white crystals m. 140.5–141.5°C]. This component gave intense blue fluorescence when treated with strong alkali, and resembles umbelliferone, which is 7-hydroxycoumarin ($C_9H_6O_3$, m. 224°C, acetyl deriv. white needles m. 142°C.). (c) A compound $C_{19}H_{22}O_2$ termed solid B, consisting of yellow crystals [m. 66.8–67.8°C, m. wt. 298.37]. (d) A substance termed solid A, $C_{28}H_{14}O_{10}$ [m. 291.5–293.5°C, m. wt. 510.39, acetyl deriv. white cryst. flakes, m. 174–175°C]. Solid B is insoluble in water, alkalis, and dilute HCl. It is soluble in sulfuric acid and in phosphoric acid. It does not contain OH groups. Tests for CO groups gave uncertain results. Solid A when heated with Zn dust and dilute alkali gave a deep red color, similar to that given by antraquinone.



umbelifferone

The method of Taub and Zweig for obtaining wax crystals was employed by Hugh using isopropanol as the solvent for grapefruit peel wax. The purified wax crystals melted between 66.5 and 67.2°C, and have an empirical formula of $C_{31}H_{36}O_3$. The substance has an acid value 1.37 saponification number 137.50, and iodine number 96.09. When treated with bromine in CCl_4 solution it forms a derivative $C_{32}H_{40}H_7O_5$ (m. 148–149°C).

WAXES IN SEED OILS AND LIQUID WAXES FROM SEED

When the seed of a plant is pressed the oil obtained generally consists of mixed glycerides, both saturated and unsaturated, and contains only a minute amount of wax, that is, less than one per cent. The wax is not economically recoverable unless large tonnages of the seed are expressed for oil, or unless the press cake, which consists of the hulls after pressing, contains a sufficient amount of wax to make its extraction with an organic solvent worth while. The seed of the shrub *Simmondsia californica*, peculiarly, is rich in an oil which is free from glycerides and hence constitutes a *liquid wax*.

Wax of Safflower

The petals and seeds of the safflower, *Carthamus tinctorius*, and of the wild safflower, *C. oxyacantha*, of the family order Compositæ, native of India, contain waxy matter as a constituent of the oil derived from them. The nonsaponifiable wax (m. 65°C) from the petals of *C. tinctorius* amounts to 13 grams per 4 kg. The wax consists principally of hydrocarbons C_{29} and C_{31}.

One of the earliest recorded waxes from a seed oil is that of the safflower. The plant *C. tinctorius* is cultivated extensively in India for the preparation of saffron yellow dye. Safflower oil is a drying oil. It is heated by the natives to obtain an oil suitable for the preservation of leather vessels, ropes, etc., making them highly resistant to water penetration. The boiled oil has a specific gravity (d^{25}) of 0.9634, saponification number 188, and iodine number 129.

When the oil expressed hot from the seeds of the wild safflower is boiled in earthernware vessels for 12 hours, and then placed in flat dishes partly filled with cold water, it solidifies to a thick jelly-like mass termed *roghan* (Afridi wax). According to Lewkowitsh[158a], this boiled oil is employed by the natives in Lahore, Delhi, Bombay, and Calcutta for the manufacture

of Afri wax linoleum. Roghan is also used by the natives for drawing artistic designs on woven cloth. Finely pointed staves are dipped in the roghan, drawing it out into very fine threads which are deposited on the cloth. When completely dry it forms an indelible pattern.

Wax of Sunflower Seed Oil

The seed oil of the common sunflower, *Helianthus annuus* L., family Compositæ, contains a minute amount of wax. The peculiar circumstances under which the wax was discovered were related by Barenther[20] in Germany in 1923. He stated, "An isolated tank of sunflower oil, from the center of which oil was withdrawn while fresh oil (10 carloads) was pumped in on top, showed at the end of the season that the oil at the bottom became turbid and gelatinous at 30°C." The sedimentary substance was the accumulation of the deposition of wax from the 10 carloads of oil. Barenther isolated the wax and found that it consisted largely of *ceryl cerotate*. The wax amounted to 0.14 per cent on the basis of the residual oil left in the tank. The source of the wax was traced to the hulls of the sunflower seed, which contain 10 per cent of wax. The wax separated from the oil during cold weather. Ceryl cerotate has the formula $C_{52}H_{104}O_2$, and melts at 84°C. Another constituent of the wax is *sitosterol*. It should prove economical to recover wax from whole sunflower seed with a solvent such as "Skellysolve B" before pressing, or to recover the wax from the presscake.

Wax from Linseed Oil

The seed oil of the common flax, *Linum usitatissimum* L., family Linaceæ, contains a minute amount of wax. Jacobsen[119] discovered the wax in edible linseed oil in 1922. When the "crude" was pressed from La Plata seed and at once refined, deodorized and cooled, it clouded when kept at 12–15°C. This cloudiness proved to be a substance insoluble in cold ether, ligroin, and acetone, and hence was easily separated. About 10 tons of the cold oil was filter-pressed, the cake extracted with ether to remove all oil, and dried. The amount of crystalline material thus obtained was 0.01 per cent of the original oil.

After careful filtration at 105–110°C the waxy material was analysed and gave the following constants: density ($d^{14.4}$) 0.977; melting point 76.6°C; refractive index (n_D^{80}) 1.4437; iodine number (Hubl-Waller) 10.6; saponification number 80.9; R-M number 0.09; Polenské number 0.05; acid value 0.0; acetyl number 6.3; unsaponifiable 43.14 per cent. The unsaponifiable contained no phytosterols nor hydrocarbons; it had an acetyl value of 128.4, and melted at 77.5°C. This was identified as *ceryl alcohol*. Jacobsen gave the composition of the wax as *stearic acid* 18.7 per cent, *cerotic acid* 32.5 per cent, *ceryl alcohol* 43.1 per cent, hydrocarbons 7.0 per cent. The wax

is not identical with flax wax (see p. 201), and resembles somewhat a wax separated from coconut oil. The wax consists chiefly of *ceryl cerotate.*

Jojoba Wax

Jojoba wax, or jojoba (pronounced hohóba) oil, is derived from the coffee-bean-like seed of the jojoba, *Simmondsia chinensis* (var. Californica), or *Simmondsia californica* Nuttall (*Buxus chinensis* Link), of the family order Buxaceæ. The jojoba, or simmondsia, is a wooden evergreen shrub, a few feet in height, which grows in abundance on rocky hillsides in Arizona, near Tucson or elsewhere, and in western Mexico, over an area roughly estimated by Mirov to cover 70,000 square miles. Mirov[190a] relates that a sizeable plantation made near Florence, Arizona, during World War II was later abandoned. A smaller experimental plantation established at Riverside, California, in 1944 is said to be fruitful. The plant is dioecious, i.e., male and female flowers are borne on separate bushes. It is a browse species capable of withstanding heavy grazing. The seed, one to the capsule or pod, is dark brown in color. Centuries ago the Indians of Baja California highly prized the jojoba for food and the oil as a medicine and as a hair restorer.

The seeds on pressing yield an oil which in some respects is not unlike sperm oil. The peculiar composition of jojoba oil, since it contains no glyc-

After A. E. Hoyle

FIGURE 10. Flowering shrub and fruit of *Simmondsia californica* Nuttall.

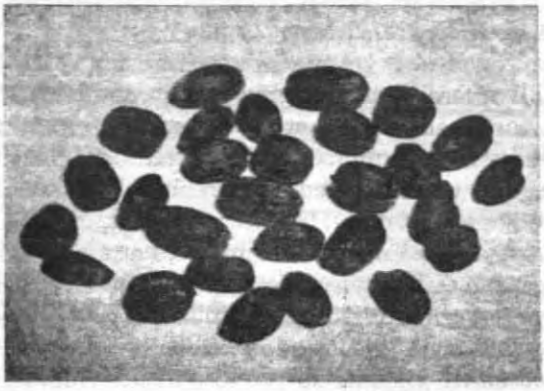


FIGURE 10a. Coffee-bean-like seeds of the jojoba have a thin, dark-brown pericarp which covers a white perisperm rich in liquid wax.

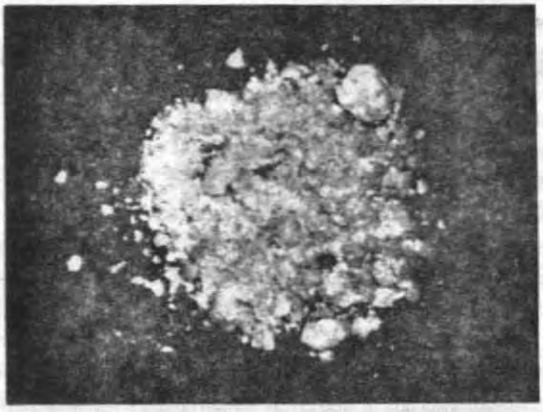


FIGURE 10b. Highly lustrous, pearly white, crystalline laminae of hydrogenated liquid wax. The solid wax melts at 70°C (158°F).

erides, places it in a category of liquid waxes. It is composed almost entirely of high molecular weight monoethylenic acids and alcohols combined as esters. That the oil is a liquid wax was first discovered by Greene and Foster[60a] in 1933, who were prompted to determine its chemical composition because of references to its medicinal and culinary use.

According to Markwood[179] the seed of jojoba, bucknut, goatnut, sheepnut, etc., as they are provincially called, contain 50 per cent or more of oil. Ordinary cottonseed crushing equipment serves to expel the oil. On a small scale it is more convenient to operate by solvent extraction, preferably using light petroleum solvent, extracting the nuts after they have been ground. The solvent is then distilled off, and a residual oil of a slightly yellowish color is obtained. The residual meal from expression or extraction of the oil contains 30–35 per cent protein and is quite acceptable as a livestock feed material. Most of the color of the oil can be dispelled by heating the oil for a short time to about 288°C (550°F).

The possible development of *Simmondsia* as a domestic crop in some areas

of the United States should, according to Daugherty and co-workers[65a], be given careful consideration. Small-scale plantings have indicated that the plant grows well under cultivation and produces larger nuts and higher yields than in the wild. The yield of oil received per acre would be several times that obtainable from other oilseed crops. Quantities of nuts, collected by hand labor, have been shipped to Europe from Mexico, attesting the feasibility of handling on a commercial scale. The seed are one-half inch long and three-eighths inch across and 35 seeds make up an ounce.

Composition of Jojoba Oil. McKinney and Jamieson[186] obtained 3 liters of a light-yellow limpid oil by grinding 25 pounds of seed, from the State of Sonora, Mexico, in a Hobart mill, and then extracting by cold percolation with petrolic ether, followed by removal of solvent and careful evaporation. They obtained the following characteristics of the oil: specific gravity (d^{25}) 0.8642; refractive index (n_D^{25}) 1.4648; iodine number (Hanus) 81.7; acid value 0.32; saponification number 92.2; unsaponifiable (I no. 77.2, acetyl val. 171.8) 48.3 per cent; saturated acids 1.54 per cent; glycerol none; iodine number of total carboxylic acid 76.1; and neutralization number of acids 172.0. Physical and chemical properties recorded by Daugherty and associates include: melting point 11.2–11.8°C; solidifying point 6.7°C; flash point (C.O.C.) 555°F; fire point (C.O.C.) 640°F; viscosity S.U. at 100°F 127 seconds; viscosity S.U. at 210°F 48 seconds; viscosity index (Dean and Davis) 173; color number (A.S.T.M.) 2; pour point 10°C; specific gravity (d_{25}^{25}) 0.8635–0.864; density (d^{25}) 0.8642–0.8990; acid value 0.23–0.57; saponification number 92.2–95.0; iodine number (Hanus) 81.7–88.4; acetyl value 6.8; R-M number 0.70; Polenské number 0.31; iodine number of unsaponifiables 77.2–80.2; acetyl number of unsaponifiables 172; soluble acids (as butyric) 2.43 per cent; insoluble acids 59.43 per cent.

The acetyl and iodine numbers of the unsaponifiables indicated to McKinney and Jamieson[186] that jojoba oil consists very largely of unsaturated alcohols (48.3%), and they found no saturated alcohols or hydrocarbons. The unsaponifiables were completely hydrogenated by Adam platinum catalyst, and then, by oxidation with chromium trioxide in glacial acetic acid, conversion by calcium to calcium salts, and hydrochloric acid decomposition of the latter, the fatty acids were recovered and purified by crystallization from alcohol. The fatty acids melted at 68.4–69°C. The mean molecular weight of 335, based upon the neutralization value 167.5, indicated behenic acid, thus establishing docosenol as the chief alcohol component of the unsaponifiable matter.

A 100-gram portion of the original oil was saponified, the acids converted into their calcium salts, and the fatty acids liberated therefrom by hydrochloric acid and then taken up with ether. The major portion of the un-

saponifiables separated as an upper liquid phase, from which later on 10.3 grams of higher fatty acids were obtained. Upon evaporation of the ether 43.2 grams of acids were obtained. These acids were converted to potassium salts, then to ethyl esters, which were fractionally distilled under reduced pressure from a Ladenburg flask. Four fractions, I, II, III, and IV, were obtained. The first fraction was redistilled to yield other fractions. Fraction Ia was hydrogenated and from this fraction was recovered pure eicosanoic acid, and small amounts of stearic and palmitic acids, originating from the *eicosenoic*, *oleic*, and *palmitoleic acids* in the oil.

About two grams of the esters of fraction II were hydrogenated and saponified, and the fatty acids liberated and crystallized from alcohol. The first crop of crystals were identified as eicosanoic contaminated with a little behenic acid, originating from the eicosenoic and *docosenoic acids* in the oil. Fraction IV when hydrogenated also proved to be a mixture of eicosanoic and behenic acids, the behenic acid being the principal constituent. Fraction III was similar.

The second portion of fatty acids (10.3 grams) separated from the unsaponifiable matter was converted into their crystal esters in the usual manner and the resultant esters were distilled under diminished pressure from a small Claisen flask equipped with a fractionating column. An examination of the saponified products revealed about one-third of unsaponifiable. The latter was separated, and after hydrogenation crops of crystals containing 50:50 molar mixtures of eicosanoic (C_{20}) and behenic (C_{22}) acids were obtained. These acids had a mean molecular weight of 326, and a melting point of 70.8°C.

The unsaponifiable fraction (49.6 grams) separated from the 100-gram portion of jojoba oil was refluxed for several hours with a large excess of acetic anhydride. The unreacted acetic anhydride was decomposed with water, and the separated alcoholic acetates were washed free of acetic acid. The dried acetates (51.9 grams) were distilled to give fractions I to IX plus residue (x). From the iodine numbers, refractive indices, acetyl values, and melting points of the hydrogenated acetates, the presence of *eicosenol*, *docosenol*, and *hexacosenol* was definitely established as the alcohol components of jojoba oil. Hexacosenol is the only unsaturated alcohol of the components that is solid at room temperature.

The percentage chemical composition is reported as saturated acids 1.64; *palmitoleic acid* 0.24; *oleic acid* 0.66; *eicosenoic acid* 30.3; *docosenoic* acid (erucic) 14.2; *eicosenol* 14.6; *docosenol* 33.7; and *hexacosenol* 2.0. Green, Hilditch and Stainsby[90] state that the chief acid is $\Delta^{11,12}$-eicosenoic acid; $\Delta^{13,14}$-docosenol and $\Delta^{11,13}$-eicosenol have been identified as the alcohols; 11,12-*dihydroxyeicosanoic acid* (m. 130.5°C) is also identified.

Uses of Jojoba Wax. Jojoba oil is said to be used by the Indians as a

hair dressing. It has culinary value as an additive to vegetable oils of the usual glyceride composition as a stabilizer against rancidity. The Northwestern University Medical School has been reported as using jojoba oil as a carrier for medicinals injected by needle.

Markwood[179] first noted the stability of the oil to heat, and states that it can be repeatedly heated to 550°F without any apparent decomposition, thus making it suited as the fluid medium for an instrument such as a melting-point apparatus, and that it is superior to various organic synthetics for that purpose. Jojoba oil is excellent for liquid heat transfer, particularly where heat must be carefully controlled. It is valuable for lubricating delicate mechanisms.

Jojoba oil can be sulfurized up to 30 per cent sulfur, and will thus yield a high-pressure lubricant, similar but superior to sulfurized sperm oil. In preparing sulfurized jojoba oil Wells[318] adds the sulfur in four portions on the up-heat between 255–400°F; then the reaction mixture is reheated for 20 minutes to insure liquid consisting on cooling, cooled to 250°F, and aerated. Jojoba oil can be polymerized into a tacky-rubbery mass, so-called "factise," and is soluble in solvents such as benzene or gasoline, in contrast to other factises; this property makes it of value for rubber dispersions and for linoleum. The factise of jojoba oil is said to be of value for chewing gum.

The human digestive system is not constructed to make use of waxy materials and so jojoba oil is not suitable as a food. However, its use has been suggested for salad dressings when and where a low caloric intake is needed. The oil is a suitable carrier for medicinals that must pass through the stomach into the small intestines before assimilation. It is useful as a stabilizer of penicillin products, being the best liquid wax for the purpose. It will inhibit the hydrolysis of vitamin A ester, and has an intense inhibitory action on the growth of tubercle bacilli, since it tends to penetrate the wax sheaths of *Mycobacterium tuberculosis*.

The United States imports about 30 million pounds of sperm oil per year at a price of about 13½ cents per pound. However, such imports have dropped to less than a million pounds in war years, creating great shortages. It is believed that at an estimated price of 11 cents per pound jojoba oil would serve as a stable domestic source of an oil of the sperm type.

Hydrogenated Jojoba Wax. Jojoba seed oil can easily be hydrogenated by a process similar to hydrogenation of cottonseed oil in the preparation of modern shortening. The resultant product consists of highly lustrous, pearly white crystalline laminae. The solid is very hard and melts at 70°C (158°F). Various uses have been suggested for the solid wax, e.g., as an ingredient in polish waxes, carbon paper, and penicillin drugs; for the waxing of fruit and the impregnation of heat-resistant paper containers; and as an exterior coating for candles. It is said that candles made from it burn with a brilliant flame and do not smoke.

Availability of Jojoba Oil. Attempts to collect large quantities of nuts from wild bushes have not been successful. The bushes are scattered and heavily browsed. Seed production is uncertain, the nuts are small in size, and the natives are reluctant to gather them. Cultivating the shrub as is being done at the Eddy plantation at Riverside, California, would assure a constant supply of nuts for oil production. The plant also offers a thick cover in the desert where cover is at a premium, and could serve as a soil-binding plant; for nut production it would need protection from overgrazing. Under cultivation the yield of nuts is higher and the seeds larger than from wild bushes[190a].

Wax of Indian Corn

The whole seed of waxy and of yellow corn, *Zea mays* L., when extracted with solvent ("Skellysolve B"), yields only 0.01 and 0.03 per cent of wax. The seed is protected from water damage by a natural resin known as mazein, or zein, rather than by wax; hence the amount of wax is small indeed. However, because of the vast amount of corn which is processed for oil, wax in appreciable amount is encountered in the sludge that settles out in chilling crude oil from Indian corn. The wax can be separated from the corn oil foots by treating it with an equal volume of ligroin to dissolve out the residual oil, and then centrifuging out the waxy mass. Shriner *et al.*[252] dissolved this waxy mass, or thick semisolid paste, in hot ligroin, filtered the solution, and allowed it to cool. About 220 grams of solid matter were obtained from 13.5 kg of the original sludge. This material still contained some oil and was recrystallized from amyl alcohol; boiled with acetone, in which the wax is insoluble when cold; filtered; and then finally recrystallized from ligroin, from which it separated in feathery crystals (m. 81–82.5°C). The yield was 120 grams or 0.9 per cent of the sludge. The crystals had a molecular weight of 778.8.

Jamieson[119a] reported the following analytical constants for corn oil wax: acid value 1.9, saponification number 120.3, acetyl value 0.4, iodine number (Hanus) 42, unsaponifiable 36.46 per cent. The unsaponifiable contained about 4.5 per cent of *myricyl alcohol* (m. 84–85°C) and 31.9 per cent of *ceryl alcohol* (m. 79°C). The wax was of a light brown color, but after one crystallization from alcohol, chloroform, or petrolic ether, gave in each case a pure white product with a melting point of 80–81°C.

The wax examined by Jamieson contained chiefly esters of ceryl alcohol, but this wax was obtained upon the long standing of a huge quantity of the highly deodorized corn oil.

Shriner and his associates[253] stated that corn oil wax is insoluble in cold ether, alcohol, ligroin, amyl alcohol, and benzene, but it is somewhat soluble in carbon tetrachloride and chloroform. A chloroform solution of the wax is optically active. The wax upon hydrolysis yields *myricyl alcohol*, which

when recrystallized from ethanol and benzene 1:1 and from ligroin, melts 87–88°C. Shriner pointed out that the melting point of myricyl alcohol is often given in the literature as 85°C, and also noted the similarity of the myricyl alcohol obtained from corn wax to that prepared from beeswax. The presence of a phytosterol in corn wax is also indicated, probably *stigmasterol*.

The fatty acids in corn wax were separated by acidifying the soap solution, freed from myricyl alcohol, with HCl, and removed as a cake after the mixture had cooled. They were then recrystallized from alcohol and acetone, after which the acids melted at 74°C and had a neutral equivalent of 357. They were esterified by refluxing with methanol and concentrated sulfuric acid. The ester formed an oily layer and when chilled was separated, dried, and distilled. The acids were then isolated from their methyl esters. Both *n-tetracosanoic acid* and *isobehenic acid* were positively identified. Hence the solid matter separated from corn oil consists largely of *myricyl esters* of *tetracosanoic* and *isobehenic acids*, and not an ester of *n*-tricosanoic acid. *Hentriacontane*, *sitosterol*, and *stigmasterol* have been reported as constituents of the crude wax.

Koryan (Kaoliang) oil is pressed from Koryan corn of Manchukuo, the yield being 3.3 per cent. This oil contans 7.6–8.6 per cent of unsaponifiable matter which when extracted with ether gives 2 per cent of *takakibyl alcohol*, $C_{44}H_{89}OH$; 12 per cent of *koryanyl alcohol*, $C_{28}H_{57}OH$ (montanyl alcohol?); 21.6 per cent *sitosterol*; and 63 per cent of a mixture of *cetyl alcohol* and a cyclic alcohol, $C_{30}H_{48}O$. The extract with benzene yields 6 per cent takakibyl alcohol, 28 per cent koranyl alcohol, and 50 per cent of sitosterol, cetyl alcohol, etc.

In the pollen of Japanese white flint corn, *Zea indurata*, there is a waxy lipid material which consists largely of *phytosterol palmitate* (m. 88–88.5°C), which Anderson[3] hydrolysed into *palmitic acid* (m. 62.5°C), and two *phytosterol* fractions melting at 122° and 136.5°C respectively. Anderson also found *n-nonacosane*, $C_{29}H_{60}$; an unidentified alcohol, $C_{30}H_{61}OH$ (m. 136°C); and a phosphatide containing 4.09 per cent phosphorus.

Anderson later found that the endosperm of corn contains some free *phytosterol* (m. 137–137.5°C), and rather large quantities of ordinary *sitosterol*, and the optically active *dihydrositosterol*, $C_{27}H_{47}OH \cdot H_2O$ (m. 140–141°C).

Wax of Celery Seed

The seed of wild celery, *Apium graveoles* L., has been reported to contain a very small amount of wax, recoverable from the sludge which settles out from the commercially extracted celery seed oil, prepared by the alcoholic extraction of ground celery seed originating from France or India. It has a

melting point of 99.4°C, acid value 25.6, saponification number 211.3 and iodine number 47.3. A recent investigation of the so-called wax made by McBeth[154a] has shown this by-product to be a gum rather than a wax. It contains no wax in significant amount, and is soluble in very dilute nitric acid.

Soybean Wax

Soybean wax is derived from the seed of *Glycine soja* (*Soja hispida* Moench), called in Japan *miso*, and can be obtained from the press cake by extraction with a suitable solvent.

Wax extracted from the settlings of winterized soybean oil contains esters, and free alcohols inclusive of sterols. The wax contains no hydrocarbons. It amounts to about 0.002 per cent of the original oil. The wax contains about 10 per cent of free alcohols, ranging from C_{32} to below C_{28}, while the acids of the esters have an average chain length of 22 carbons. No free acids are present; two phytosterols are indicated as components.

In the high-pressure hydrogenation of soybean oil Shinosaki and Kubo[251] found that at 350°C an almost entirely waxy substance was formed. The manner in which the wax ester forms appears to be a function of the reaction temperature. At temperatures above 300°C, the soybean oil glyceride decomposes, resulting in the formation of higher alcohols; and above 350°C unsaponifiable matter comprising hydrocarbons, inclusive of *octadecane*, is produced. The esterified wax substance is comprised largely of an *ester* of *stearic acid* and *octadecyl alcohol*, which ester has the following constants: melting point 58.5°C; saponification number 102.4; acetyl number 0.9; iodine number 0.4; density (d^{65}) 0.8296; refractive index (n_D^{65}) 1.4419. The catalyst used in the hydrogenation was copper carbonate on infusorial earth, and the pressure in the autoclave was 125 kg per sq cm.

Soybean oil contains *γ-sitosterol*, a stereoisomer of *β-sitosterol* (22-dihydrostigmasterol). *Stigmasterol* is a prominent component of soybean oil, as well as *lipositol*, an inositol-containing lipid containing phosphorous. It is obvious that these sterols and the phosphatide would also be at least minor components of the lipid wax.

Sesame Seed Oil Wax

A wax has been reported as constituting the chief component of a sludge of the "black" seed oil derived from the oriental sesame, *Sesamum indicum* L., a species of herb growing in Africa. The waxy matter is responsible for the cloudiness which develops in oil that has been doubly refined, in the course of a few days. The saturated wax has a melting point of 80°C, and is optically active. It is insoluble in ethyl ether; soluble in hot absolute ethanol and in hot benzene. The waxy substance is free from sterols.

Rambutan Seed Wax

The seed of the rambutan (i.e., hairy) tree, *Nephelium lappaceum* L. of India, yields a wax or vegetable tallow. The tallow when hydrolyzed produces fatty acids from which may be crystallized through petrolic ether extraction 20 to 21 per cent of *eicosanoic acid* (m. 74.5–75°C). The seed provides a good source for the latter acid.

Wax of *Spiraea Ulmaria* Seed

The seed of the European meadowsweet, *Filipendula ulmaria* (*Spiraea ulmaria*), contain 17 per cent of a drying oil, resembling linseed oil. The oil contains 17 per cent of a wax which has an extremely high melting point (240–260°C), a saponification number of 100, and yields a mixture of higher alcohols (m. 114–154°C) and acids (m. 169–170°C) on saponification. The acids have not been identified.

Chinese Tallow Tree Wax

The seed of the chinese tallow tree, *Sapium sebiferum* (L.) Roxburgh (*Stillingia sebifera* Michaux), a member of the Euphorbia family, yields a waxy tallow, of considerable economic value in China where it is made into candles. The plant is a native of the tropics of both hemispheres. It is grown in China, India, and Japan, and has been cultivated in the vicinity of Houston, Texas, and elsewhere in the southern states as ornamental, because of the beauty of its foliage which takes on a bright red hue in the autumnal season. The tree common to the central regions of China provides the stillingia oil of commerce, a wood for engraving, the tallow prized for candle-making (in China), and a protein which may be extracted from the kernel. Stillingia oil is a drying oil of considerable value in the paint industry.

The fruit, which grows at the end of the branches, is a blackish capsule of about 15 mm diameter, usually filled, in maturity, with three whitish seeds. The husk of the pod falls to the ground, leaving the pea-size seed exposed for harvesting. In order to prevent mildewing of the seed coat the branches are cut off soon after the pods open. A tree produces about 70 pounds of seed the first year of fruiting, and more seed each year thereafter. The seed consists of an endosperm with embryo at one end, surrounded by a shell which has a heavy outer coat of tallow and fiber. The embryo is rich in protein flour and stillingia oil. The seed contains 24 per cent of tallow, and 20 per cent of the drying oil. Potts and Bolley[211] report that the seed coat itself contains 74.7 per cent tallow, and the hull or shell 34.9 per cent.

The seed is treated with hot water to decoat it and remove the tallow, which when fiber-free constitutes 23.4 per cent; the fiber removed from the tallow amounts to 6.6 per cent. Bolley and McCormack[82] reported that the processes which they used to separate the seed from the Chinese tallow tree, grown in Texas, yielded 21.0 per cent tallow, 7.5 per cent kernel, 21.4 per

cent drying oil, 36.2 per cent shell, and 13.9 per cent fiber and water-soluble material.

At the College Station of the Agricultural and Mechanical College of Texas an analysis by Potts and Bolley[211] of the tallow had shown an acid value 11.92, saponification number 221.5, iodine number 10.5, Hehner number 91.92, and a melting point 56.8°C.

The native tallow of the Chinese tallow tree, which tallow is called *pi-yu* by the Chinese, or *Nankin-haze* by the Japanese, appears to have a larger proportion of unsaturated fatty acids than the tallow produced by the same species of tree grown in Texas, as shown by the higher iodine number. This difference may be due to an inferior method of refining the pi-yu. There are two grades of the latter, namely "prima," a yellowish white solid; and "secunda," a more yellow one. The density ($d^{15.5}$) of the "prima" is 0.884–0.904, saponification number 206, iodine number 19–61, melting point 36–47°C, and acid value 4.2–14.7. Nakamori[197a] gives the density ($d^{15.5}$) of the "secunda" as 0.893, saponification number 204, iodine number 83, acid value 1.5. The fatty acids of "prima" give a titer of 53.5° C, neutralization value 222.9, and iodine number 31.1; fatty acids of "secunda" give a titer of 43°C, neutralization value 221.4, and iodine number 84.3.

The chemical composition of the Chinese vegetable tallow has been reported by Koyama[140] as consisting chiefly of *tripalmitin* and *oleodipalmitin*, accompanied by small amounts of the glycerides of lauric, myristic, and stearic acid. Nobori[199a] states that the fatty acids consist of 64.3 per cent *palmitic* and 35.7 per cent *oleic acid*, and traces of *linoleic* and *eicosenoic acids*. The unsaponifiable matter amounts to 0.39 per cent, which includes a *phytosterol*.

Gupta and Meara (Univ. of Liverpool, England)[94a] in 1950 reported that the tallow encasing the seeds of *S. sebiferum*, from Hong Kong, has as its chief component glycerides: *oleodipalmitin* 64, *stearodipalmitin* 13, *tripalmitin* 8, and *oleopalmitostearin* 8 per cent, with very small amounts of *oleomyristopalmitin*, *linoleodipalmitin*, and *palmitoöleolinolein*. The stearodipalmitin and oleodipalmitin occur exclusively as the symmetrical isomers. The component acids are *myristic* 0.5, *palmitic* 63.2, *stearic* 7.6, *oleic* 27.1, and *linoleic* 1.6 per cent.

According to Gupta and Meara[94a] the tallow of the Texas-grown *Stillingia* has a somewhat different composition from the Chinese-grown *Stillingia*. The chief component glycerides of the tallow of *S. sebiferum* from southern Texas are *oleodipalmitin* 51, *palmitodiolein* 29, *palmitoöleolinolein* 6, *oleomyristopalmitin* 5, and *oleopalmitostearin* 5 per cent with very small proportions of oleomyristostearin, linoleomyristopalmitin, linoleodiolein, and traces of triolein. The acid components are: *myristic* 3.4, *palmitic* 72.1, *stearic* 1.6, *oleic* 20.4, *linoleic* 1.6 per cent.

A specimen of tallow from a species of *Stillingia* known as *S. discolor*[94a]

contained a much larger percentage of unsaturated glycerides than the specimens derived from *S. sebiferum*. The component acids of the tallow of *S. discolor* are: *myristic* 1.7, *palmitic* 46.8, *stearic* 2.0, *oleic* 46.4, and *linoleic* 3.1 per cent by weight.

Uses of Chinese Tallow Tree Wax. The tallow is extensively used in China for making candles. It is said that about 21,000 tons of the tallow is produced in China each year, most of the amount for candlemaking. A thin coating of Chinese insect wax is applied to the outside surface to keep the candles from bending in warm weather. *Stillingia* tallow when properly refined is edible.

Coffee Berry Wax

The seed of coffee, *Coffea arabica* L., contains very little wax, but an appreciable amount can be recovered as a by-product when the coffee is extracted in large quantities in the Kaffee-Hag process, which provides a means of decaffeinating coffee by solvent extraction. Only the lipid wax in the outer part of the seed undergoes alteration; the true coffee fat is merely set free by roasting. The crude wax is dark gray in color and of a firm although unctuous consistency. The crude wax includes much fat (glycerides) and has the following proximate composition: water 6.3, ether extract 71.3, ash 2.1, protein 19.0, and carbohydrate 1.3 per cent. The ash, 1.64–2.10 per cent, contains 0.06 per cent of P_2O_5, 0.07 per cent of K_2O, and 1.5 per cent of Fe and SiO_2. The semicrude wax, essentially a vegetable tallow, comprises about half of the so-called coffee-bean fat, and amounts to somewhat less than 2 per cent of the roasted bean.

In 1910 Meyer and Eckert[189] reported that the fat of the coffee bean contained 21.0 per cent of unsaponifiable wax, which gave a *phytosterin* reaction, and that it seemed to contain *tannol carnaubate*. The fatty acids in the crude lipid wax consist of *palmitic* and *oleic acids*, with some *myristic* and *stearic acids*, and traces of *arachidic acid*. The oily portion of the crude contains much *linoleic acid*. There are several sterols and pseudosterols, which are known as *kahweol* (m. 143.5°C, $[\alpha]_D$ −204.5°); *cafestol*, $C_{30}H_{48}O_2$ (m. 156°C, $[\alpha]_D$ −114°); *stigmasterol* (14.5%); and *coffeasterol*, $C_{28}H_{44}O$ (m. 147–149°C), of the ordinary sitosterol type. Both kahweol and cafestol have double bonds. Wagner[306] reported finding a wax acid (m. 84.6°C) with a molecular weight of 362.4. This acid is possibly a mixture of *lignoceric* with a lesser amount of *cerotic acid*. *Phosphatides* have also been identified as components.

In view of the work of Meyer and Eckert[189] and more recently Wagner[306] and others, the chemical composition of the unrefined or semicrude coffee berry wax is beginning to become known.

TABLE 63. APPROXIMATE COMPOSITION OF SEMICRUDE COFFEE BERRY WAX

Tannol Ester of Monobasic Fatty Acid:	20 per cent
Tannol tetracosanate (tannol carnaubate?)	
Glycerides of Saturated Monobasic Fatty Acids:	50–52 per cent
Palmitin, $C_3H_7(C_{16}H_{31}O_2)_3$, 12½–14%	
Behenin, $C_3H_7(C_{22}H_{43}O_2)_3$, 1%	
Lignocerin, $C_3H_7(C_{24}H_{47}O_2)_3$, 36–37%	
Glycerides of Unsaturated Monobasic Fatty Acids:	18–19 per cent
Linolein, $C_3H_7(C_{18}H_{33}O_2)_3$, 8–9%	
Olein, $C_3H_7(C_{18}H_{35}O_2)_3$, 10%	
Free Fatty Acids:	1 per cent
Palmitic acid	
Behenic acid	
Cerotic acid	
Sterols & Pseudosterols	3 per cent
Stigmasterol, $C_{29}H_{48}O$	
Coffeasterol (m. 147–149°C)	
Kaweol (m. 143.5°C)	
Cafestol (m. 156°C)	

WAXES FROM FLOWERS

When flowers as jasmine, orange, rose, tuberose, and violet are extracted with petrolic ether, the extracts contain besides the essential oil proper, a certain amount of vegetable wax and coloring matter. The flowers are placed by the grower or perfumer in hermetically sealed cylinders and the petrolic ether allowed to run through them slowly. The last container in the row is connected with a vacuum still and the solvent distilled off and returned to the tank for reuse. The perfume remains behind in the retort and is called a *concrete*. It contains the highly odorus essence together with natural and insoluble plant waxes.

The concretes are shaken by the performance with strong and pure alcohol for 24 hours in machines called *batteuse*. The perfume and some wax is dissolved and the insoluble waxes filtered out. The alcoholic extract is then placed in a freezing mixture to separate the soluble waxes. The floral waxes are thus by-products. Flowers yield 3 per cent or less of total extract of which 70 per cent or more is wax. The waxes at times act as excellent fixing agents for perfumes, and hence concretes find a market as well as the absolute flower oils prepared from the alcoholic extracts. Concretes are also steam distilled until the residue is odorless, and the oil is recovered from the distillate by extraction with ether, in which instance the residue consists of a crude floral wax, usually highly colored.

In the Egrot steam process the flowers are put in a perforated copper basket which is lowered into a still placed over a fire. On boiling, the essential oil collects on the surface of the water, where it can be drawn off from time

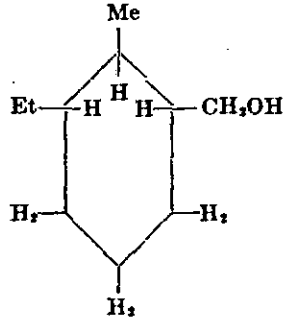
to time. The condensed water is run back into the boiler. Some of these oils in storage deposit a small amount of wax.

In the *enfleurage process*, or cold perfumery, the essential oils of the blossoms are adsorbed by a suitable fatty medium (e.g., olive oil or lard). Glycerine, soft paraffin, and vaseline have also been used in the extraction of the odoriferous principles. The fatty medium with its adsorbed perfume is then extracted with alcohol (cologne spirits), and on chilling by freezing mixtures or other means to −18°C, the fatty material is separated out and gotten rid of.

Rose Wax

Rose wax is obtainable as a residue in the solvent extraction of the essence of roses, *Rosa* spp. According to Viard[305], 1000 kg of roses (Grasse) yield 2.4 kg of concrete of which 28.4 per cent is absolute flower oil. The floral wax is a hard olive-green solid which melts at 61°C. It is completely soluble in chloroform, benzene, and petrolic ether, and partially soluble in alcohol, ethyl ether, and acetone. The following chemical constants were determined by Prophéte[218]: saponification number 29.8, acid value 3.15, ester value 26.55, iodine number 13.0, Reichert-Meissl value 1.35, Hehner number 97.4, acetyl value 31, and unsaponifiable matter 80.2 per cent.

The chemical composition of rose wax is that of straight-chain alcohols combined with fat acids, cyclic alcohols free and combined, and hydrocarbons. The cyclic alcohols (cyclonols) include *cyclodecanol* (b_{12} 125°C, m. 40–41°C). The latter has the chemical structure, $C_{10}H_{20}O$.



It also contains one or more of the following cyclic alcohols: *cyclododecanol*, $C_{10}H_{20}O$ (m. 80°C); *cyclotetradecanol* (m. 79–80°C); *cyclohexadecanol* (m. 79–80°C); *cycloöctadecanol* (m. 81°C); *cycloeicosanol* (m. 69°C). They all have estolidic properties. The acids of rose wax, such as palmitic, etc., are fully combined with alcohols or esters. The very low acid value of the wax may be ascribed to the presence of etholides, which are long-chain compounds with several carboxylic radicals but with only one acid hydrogen (see p. 62). The wax also contains a very large percentage of hydrocarbons.

TABLE 64. COMPOSITION OF ROSE WAX

Alkyl Esters of Wax Acids:	28.3 per cent
Cerylic alcohol, 3%, and	
Isocerylic alcohol, 6%, both combined with	
Soluble fatty acids, 1.6%	
Insoluble saturated acids, 10.6%	
Unsaturated acids (as oleic), 6.4%	
Alcohols, Free and *Combined* (to lesser extent):	11.2 per cent
$C_6H_{12}O$; 8%	
C_xH_y (unknown, m. 16°C), 0.5%	
Cyclodecanol (m. 43°C), 1.0%	
Cyclonols (unknown, m. 49.6°C), 1.5%	
Anolides of ω-Hydroxy Acids:	3.3 per cent
Anolide of $C_{18}H_{36}O_3$ (m. 73°C)	
Hydrocarbons:	56.5 per cent
$C_{30}H_{62}$, 6%; $C_{27}H_{56}$, 15%; $C_{26}H_{54}$, 8%; $C_{23}H_{48}$, 6%; $C_{21}H_{44}$, 2%; $C_{22}H_{46}$, 6%; $C_{20}H_{42}$, 8%; $C_{18}H_{38}$, 0.5%; not recovered, 5%	
Water:	0.68 per cent

Louveau[187] in 1931 reported indices for the wax of the Provence, or cabbage, rose, *Rosa centifolia* L. The acid and ester values were at variance with, that is much higher than, those of Prophète. In other respects, such as the melting point and hydrocarbons content, there is a fair agreement. Louveau's constants are: specific gravity (d^{15}) 0.970–0.988; melting point 59–60°C; acid value 38.5–39.4; ester value 80.8–86.7; hydrocarbons 50–52 per cent.

The composition in Table 64 is based upon the work of Prophète[219].

Wax By-Product of Rose Perfume. Straman[265] analysed and determined the constants of exhausted wax of the rose obtained from perfume manufacturers in France and Holland. The wax represents the petrolic ether extract of the blossoms after they have been extracted with alcohol for the recovery of volatile oils: specific gravity (d^{15}) 0.9290, melting point 57.5°C, acid value 3.40, ester value 23.98, iodine number 12.87, saponification number 27.38, hydrocarbons 74.2, and higher alcohols 11.7 per cent.

Wax of Druscky Rose

In a study of the chemical composition and biological role of waxes occuring in perfumed flowers, an examination of the wax of the Druscky (Druschki) rose was made by D'Ambrosio[63]. The wax is an intensely yellow, amorphous mass (m. 57–58°C), the surface of which is covered with rhombic crystals. The wax is soluble in a number of solvents, but only partially soluble in hot ethanol. D'Ambrosio found that the part which is insoluble in hot ethanol melts to an oil in the solvent, and can be separated; on cooling the separated oil precipitates out a white flaky substance (m. 71–72°C). The mother liquor on evaporation leaves a yellow wax, which melts at

71–72°C. It can only be incompletely crystallized from a benzene-petroleum ether (1:3) solution in an acicular form, indicating it to be a mixture.

From this was D'Ambrosio succeeded in isolating an acid of the composition, $C_{18}H_{36}O_3$ (m. 73°C), to which he gave the name *rosilic acid* and which he identified as *10-dihydroxystearic acid*. A dihydroxy acid identified as *9,10,-Dihydroxystearic acid* (m. 137°C), resulted from oxidation by $KMnO_4$ of the oleic acid in the wax. From the mother liquor of the barium salt of rosilic acid was isolated an acid which melted at 70°C and had an acid number of 3.9. This on saponification gave rosilic acid, and proved to be an *etholide* of 5 carboxyls. There was also present a compound composed of acicular crystals (m. 119°C) which could not be identified. A secondary alcohol, $C_{17}H_{36}O$ (m. 60–61°C), isolated from the oily wax (m. 57–58°C) component of the hot ethanol insoluble portion, was shown to have the composition $Me(CH_2)_7CH(OH)\cdot(CH_2)_7Me$, *d-heptacosan-9-ol*.

Wax from Violets

Viard[305] reported that from a 1000 kg lot of violet leaves he had obtained 1.070 kg of extractives with petrolic ether. The essential oil obtained from the extract by steam distillation amounted to 1.68 per cent. The residue comprised wax and coloring matters. Wax obtained as a residue in the extraction of the essence from the English sweet violet, *Viola odorata* L., with volatile solvents, has been assayed by Louveau[167]. The following constants have been recorded: density (d^{15}) 0.962–0.966; acid value 12.2–14.4; ester value 53.2–55.0; melting point 58–61°C; hydrocarbons 44–45.8 per cent.

Straman[265] obtained the following constants and constituents from the examination of the exhausted wax by-product of perfume manufacturers in France and Holland: specific gravity (d^{15}) 0.963, acid value 12.01, ester value 53.68, iodine number 17.28, saponification number 65.69, melting point 58°C, hydrocarbons 46.95 per cent, higher alcohols 10.25 per cent, saturated acids 34.99 per cent, and unsaturated acids 5.80 per cent.

Giacomello in Italy reported that the unsaponifiable fraction of the wax of violets, *Viola* spp. (L.), contains a wax of the composition $C_{30}H_{50}O$ (m. 284.5°C, d^{15} 1.076), and has been identified as a triterpene with an esterogenic action. *Nonenol*, C_9H_7OH, has been reported by Taki *et al.*, as a constituent.

Mimosa Floral Waxes

Several species of Acacia, family order Mimosaceæ, yield floral waxes. Straman[265] analysed and determined the constants for the wax of sweet acacia, *Acacia farnesiana* Willd. He obtained samples of the wax which represented the petrolic ether extract of the blossoms after it had been ex-

tracted with ethanol for the recovery of the volatile oil of mimosa. The characteristics of the wax are as follows: specific gravity (d^{15}) 0.960; acid value 16.42; ester value 89.31; iodine number 34.58; saponification number 105.73; melting point 59°C; hydrocarbons 51.90 per cent; higher alcohols 23.90 per cent; saturated acids 14.20 per cent; unsaturated acids 8.00 per cent. Louveau[157] reported the constants for the wax of cavenia acacia, *A. cavenia*, to be as follows: specific gravity (d^{15}) 0.946; acid value 6.3–7.0; ester value 52.5; hydrocarbons 29.8 per cent. The constants for silvergreen-wattle acacia, *A. dealbata*, are: specific gravity (d^{15}) 0.962–0.969; acid value 24.8–25.2; ester value 78.9–89.0; hydrocarbons 47–49 per cent. The saturated acids of mimosa wax are *palmitic, stearic* and *cerotic*. The chief hydrocarbon is *hentriacontane*. Straman states that glycerides are absent.

Kurtz, Jr.[148] dried several species of acacia, extracted them with petrolic ether, and separated the extract into wax and nonwax fractions with acetone. Small amounts of wax, a fraction of one per cent, were obtained from catclaw acacia, *A. greggi*, *A. Gray*, vernicosa acacia, *A. vernicosa*, and miscat acacia, *A. constricta*. The iodine number of the wax of *A. greggi* was only 0.4.

Wax of *Butea* Flowers

The flowers of the dhak or palas tree, *Butea monosperma* (*Butea frondosa* Roxb.), contain a small amount of wax. The palas tree, which is indigenous from India to Burma, furnishes from its inspissated sap a gum, red in color, and known as *Palas kino* or *Bengal* gum. The seeds of the tree are the source of *moodooga oil*, and the flowers (keeso, teeso) are used for dyeing. The tree also yields a lac. When the dried flowers are extracted with petrolic ether, and the extract dried and taken up with acetone, there can be obtained 0.75 per cent of a colorless wax, according to investigators at Andhra University, Waltair, India. The dried, powdered flowers when extracted with carbon tetrachloride yielded 0.35 per cent of waxy material, which after repeated solution and precipitation with ethanol, yielded a wax with the following constants: specific gravity (d^{15}) 0.980, acid value 6.2, saponification number 40.8, iodine number 1.2, and unsaponifiables 70.0 per cent. From the wax was isolated by crystallization from ethanol and ether an alcohol (m. 83–85°C) which proved to be *myricyl alcohol*. Fatty acids identified by its investigators were *palmitic, stearic, arachidic, behenic*, and *lignoceric*. *Cerotic acid* is also known to be a constituent. *Sitosterol* is thought to be a component. The wax has a melting point of 73–76°C.

Jasmine Flower Wax

The large-flowered white jasmine, *Jasminum grandiflorum* L., is extensively used in the manufacture of perfume. According to Viard[305], when

jasmine flowers are extracted with petrolic ether, 3 kg of extractive solids are produced from 1000 kg of blossoms. The essential oil content of the extract is determined by evaporating the solvent, steam distilling the concrete until odorless, and recovering the oil from the distillate by extraction with ether. Viard found that the extract of jasmine flowers thus contained 8 per cent of oil. The balance of the extract consisted largely of wax and coloring matters. It appears that the waxes at times act as excellent fixing agents for the perfume, but are only slightly soluble in the strongest alcohol. The commercial method for removing the wax from the perfume concrete has already been described.

In 1909 Radcliffe and Allan[221] gave the following analytical characteristics for jasmine flower wax: It is hard, and yellowish brown in color; titer 56–57°C; Zeiss butyro-refractometer readings 30 at 84°, 33 at 74°, 36 at 70°, 38 at 65°, 40 at 62°, and 44 at 56°C; acid value 2.8; saponification number 65.8; iodine number (Wijs) 52–53. The fatty acids have a mean molecular weight of 398 and an iodine value of 39. The unsaponifiable matter yields white needles of alcohols (m. 64°C, acetyl derivative m. 45°C).

Straman[265] has given the characteristics and composition of jasmine floral wax obtained from the petrolic ether extract after exhaustion of the perfume by alcohol. They are as follows: specific gravity (d^{15}) 0.932; acid value 5.4; ester value 55.5; iodine number 40.26; saponification number 60.9; melting point 60°C; hydrocarbons 49.85 per cent, higher alcohols 14.35 per cent, saturated acids 21.31 per cent, unsaturated acids 14.50 per cent.

Louveau[167] reported the following analytical constants for jasmine floral wax: density (d^{15}) 0.950–0.971; acid value 6.0–7.6; ester value 56.8–60.0; melting point 61–64°C; hydrocarbons 40–44 per cent.

Jasmine flower wax has been prepared in Japan from the shuei flower, i.e., the sweet-scented yellow jasmine, *Jasminum odoratissimum* L. The flower is cultivated in Formosa, and is noted for its fragrance. From 90 kg of fresh blossoms, Tsuchihashi and Tasaki[278a] obtained 250 grams of essence by extraction with petrolic ether. The yield of essential oil from the essence was 0.116 per cent on the flower basis, and the yield of flower wax was 0.166 per cent.

Shuei flower wax has a specific gravity (d_{15}^{100}) of 0.8259 when melted; a refractive index (n_D^{60}) of 1.4622; an optical rotation ($[\alpha]_D^{15}$) of 0.11; acid value 1.25; saponification number 67.5; unsaponifiable 67.1 per cent; iodine number (Hübl) 100; Reichert-Meissl number 1.0; and melting point 55–57°C. These investigators reported the wax to contain 67 per cent of *triacontane*, $C_{30}H_{62}$.

The esters of floral waxes of the above descriptions are believed to comprise higher alcohols (C_{20}–C_{28}) with *palmitic, stearic,* and *cerotic acids*. The chief hydrocarbon constituent is *hentriacontane*, $C_{31}H_{64}$.

Sweet Mock Orange Flower Wax

When the petals of the sweet mock orange or syringa, *Philadelphus coronarius* L., are extracted with petrolic ether there is obtained 0.0784 per cent of a brown wax[239] which melts at 57°C, has a slight odor resembling jasmine, and which according to Radcliffe and Allan[22] has the following analytical constants: titer 56–57°C; Zeiss butyro-refractometer readings, 30 at 84°, 33 at 74°, 36 at 70°, 38 at 65°, 40 at 62°, and 44 at 56°C; acid value 2.8; saponification number 65.8; ester value 63. Amyl alcohol was used as a solvent for the wax in the determination of the saponification number. The iodine number is 52–53 (Wijs). The purified wax acids had a mean molecular weight of 398 and an iodine number of 39. The unsaponifiable when crystallized from ether yields a mass of white needles (m. 64°C); it contains both alcohols and hydrocarbons, including one substance which melts at 45°C. The high molecular weight of the wax acids would indicate the presence of *cerotic acid* with lower and higher homologs, combined as esters, as shown by the low and high ester values.

Lily-of-the-Valley Wax

When the flowers of the lily-of-the-valley, *Convallaria majalis* L., a perennial herb, are extracted with petrolic ether there can be recovered 0.166 per cent of a white wax, which has a characteristic odor and a melting point of 61°C. The wax contains a large amount of carbonyl compounds, according to Sabetay[238], possibly keto acids combined with ketone alcohols.

Lilac Wax

When the flowers of the common lilac, *Syringa vulgaris* L., family order Oleaceæ, are extracted with petrolic ether, there can be recovered 0.377 per cent of a brown wax (m. 44°C) which according to Sabetay[238] has an acetyl number of 15.8, and an ester value of 94.7.

Wax of Clover Flowers

The dried flowering tops of the carnation or crimson clover, *Trifolium incarnatum* L., were extracted by Rogerson[232] with alcohol, and the extract then distilled with steam to secure 0.029 per cent of essential oil. From the portion insoluble in alcohol he obtained a wax which contained *incarnatyl alcohol*, $C_{34}H_{69}OH$, an alcohol previously isolated from the wax of the humble bee (see p. 102); *hentriacontane*; *β-sitosterol* (same as that from jambul seed) [m. 135–136°C, $[\alpha]_D^{20} -41.7°$]; *trifolianol*; *palmitic*, *stearic*, *linolic*, and smaller amounts of *oleic* and *isolinolenic acids*.

Wax of Spanish Broom Flower

Spanish broom flowers, yellow blossoms of *Spartium junceum* L. (*Cytisus junceus*), are extracted with petrolic ether and the solvent then removed at

a low temperature to obtain an extract which is of value to the French perfume industry. The concrete is an oily extract which amounts to 0.09–0.18 per cent of the dried flowers. Treatment of the concrete with cold ethanol gives 40 per cent of soluble perfume, and the insoluble portion is wax. The unsaponifiable material from the broom wax is reported by Musgrave *et al.*[196a] to consist of a mixture of higher paraffins; higher aliphatic alcohols; α-, β-, and ∂-amyrin; lupeol; *β-sitosterol*; *n*-octadecane-1:18 diol and a *n*-hexacosane-1:26-diol; and two unidentified alcohols.

Wax of Pummelo Flowers

The wax of the flowers of *Citrus maxima* (*C. grandis*) has been analyzed by Yasunaga[328]. The flower wax was saponified with concentrated alcoholic KOH and the unsaponifiable matter fractionated by absorption of its petrolic ether solution through an alumina column. *Untriacontanol* (m. 80.5–81.5°C) and *sitosterol* (m. 135–136°C) were isolated from the most readily adsorbed portion. The nonadsorbed portion gave *triacontane* (m. 64–65°C), *nonacosane* (m. 62.5–63.5°C), *pentacosane* (m. 53–54°C), and *lupeol* (needles, m. 210°C). The presence of an aromatic terpene alcohol (linaloöl or geraniol) was shown in the alcohol-soluble part of both portions.

Wax of Tuberose

The tuberose, *Polianthes tuberosa* L., family order Amaryllidaceæ, indigenous to Mexico and widely cultivated for use in perfumery, contains a wax. Viard[305] extracted 1000 kg of tuberose flowers with petrolic ether and obtained 0.98 kg of extract which contained 3.34 per cent of absolute oil. Most of the extract consists of wax and coloring matters.

Wax of Hyacinth Flowers

Blossoms of the common grape hyacinth, *Muscari botryoides* Mill., or allied species belonging to the family Liliaceæ, contain a wax. The wax is obtainable by extracting the dried residue left after exhaustion of the blossoms with ethanol to produce the perfume essence. The petrolic ether extract after distilling off the solvent leaves a soft wax of greenish-yellow color, which has a somewhat larger proportion of esters of unsaturated acids, and a lower melting point, than other floral waxes.

The following constants were recorded by Straman[265] for a wax of the above description, which was secured from perfume manufacturers in France and Holland: density (d^{15}) 0.956; melting point 48°C; acid value 2.2; ester value 102.7; saponification number 104.9; iodine number 55.8; hydrocarbons 25.4 per cent; higher alcohols 25.0 per cent; saturated acids 27.7 per cent; unsaturated acids 19.1 per cent. The chief hydrocarbon is *hentriacontane;* and the acid constituents are *palmitic, stearic,* and *cerotic acids.* Glycerides are absent.

Wax of Camomile Flowers

Power and Browning[213] studied the constituents of the flowers of the Roman camomile (English camomile), *Anthemus nobilis* L. Belgian flowers were percolated with hot alcohol. The viscid extract when steam distilled gave off a volatile oil, and the residual matter consisted of an aqueous liquid and a fatty matter with resin, which could be separated. The latter when extracted with petrolic ether yielded upon saponification *triacontane*, $C_{30}H_{62}$, and *taraxasterol*, $C_{29}H_{47}OH$ (acetate $[\alpha]_D$ 102.3°). Also identified were *oleic*, *linoleic*, *palmitic*, *stearic* and *cerotic acids*. The ether extract gradually deposited a phytosterolin (phytosterol glucoside) which contained chiefly *sitosterol* and less *stigmasterol*.

Wax of *Moringa* Flowers

Rangaswami and associate[224] extracted the flowers of the horseradish tree, *Moringa plerygosperma* Gaert., with petrolic ether and obtained from the extract a wax which had a melting point of 69–72°C, acid value 10.5, saponification number 29.8, and unsaponifiable 75.5 per cent. The seeds yield oil of Ben (behen oil), although the true oil of Ben comes from a species known as the Arabian horseradish tree, *M. aptera*, native of Arabia to Abyssinia. *M. oleifera* Lam. is also given as a source of behen oil, and indirectly as a source of *behenic acid*.

Wax of *Chimonanthus* Flowers

Louveau[167a] reports that an extraction of the flowers of the wintersweet, *Chimonananthus fragrans* (*C. praecox*), with petrolic ether yields a crude wax which is comprised of paraffins (37.2%), a white wax (13.7%), and a so-called vegetable tallow (11.9%); and an oil (19%).

Wax from *Clematis* Flowers

The flowering branches of traveler's joy, species *Clematis vitalba* L., indigenous to Europe, yield a very small amount of wax. According to Tutin and Clewer[234] the plant loses 65 per cent of weight on drying. The alcoholic extract of the dried plant material was taken up with water, and steam passed through the water so as to separate the aqueous liquid from the wax-containing resin, which constituted 2.29 per cent of the plant material used. The resinous matter was dissolved with alcohol, mixed with sawdust, and dried. The dried material was extracted with petrolic ether. On the addition of ethyl ether a waxy matter deposited in the course of time. The wax when separated yielded *melissic acid* and *myricyl alcohol* on saponification, indicating the presence of an ester, *myricyl melissate*. In the unsaponifiable portion they isolated *ceryl alcohol*, *hentriacontane*, and a phytosterol, which they believed to be a mixture of *sitosterol* and *stigmasterol*. Acids (by hydrolysis of the saponifiable) identified as wax constituents are *palmitic*,

stearic, isobehenic (plates, m. 69.5°C), and *cerotic acids*, and a mixture of unsaturated acids, chiefly *linoleic*. The ether extract comprised a phytosterolin (m. 295°C), *myricyl alcohol*, a saponin (m. 235–240°C), and dextrose.

Wax of Greasewood Chamise Blossoms

A greenish-white wax may be extracted from the blossoms of the greasewood chamise, *Adenostoma fasciculatum*, of the order Rosaceae. The wax is also found in the foliage. The blossom wax has a saponification number of 127.6, the new foliage one of 126.9, and the old foliage 111.2. The blossom wax has a iodine number of 20.1, and a neutralization number of 79-2.[184a] The wax contains about 36 per cent of resin and sapogenic acid (oleanolic ?) based upon its chemical constants and physical characteristics. The blossom wax has a Fisher-Johns melting point of 194°C minimum, 207°C bulk, and 214°C maximum. It is very brittle.

When the chamise blossom wax is added to paraffine it elevates both the melting point and hardness of the latter. The durometer hardness of paraffin wax (130/133°F/A.M.P.) was elevated from 67.4 to 75.7 by the addition of 5 per cent of the blossom wax, to 80.6 by 10 per cent, and to 85.5 by 20 per cent. Additional amounts of the blossom wax give blends which are too brittle for practical purposes[184a].

Wax of Nim Blossoms

Mitra and Siddiqui[190b] in their chemical examination of the blossoms of the nim tree, *Melia azadirachta* L., which species is the source of Assam or Bengalore gum, found that the residue of the petrolic ether extractive, after steam distillation, consisted of a waxy solid. Upon saponification of the wax the unsaponifiable fraction was found to contain a steroid, which was named *nimbosterol*, and a hydrocarbon ($C_{29}H_{60}$), but no bitter principle. Nimbosterol, $C_{20}H_{34}O$ [m. 137°C, $[\alpha]_D^{27.6}$ −74° ($CHCl_3$)], can also be obtained by direct alcoholic extraction of the blossoms; the yield is 0.3 per cent by weight of the blossoms. The hydrocarbon is *nonacosane*, $C_{29}H_{60}$ [m. 64–66°C, $[\alpha]_D^{26}$ −9° ($CHCl_3$)]; the yield 0.01 per cent. The essential oil of nim blossoms is customarily known as margosa oil.

Wax of *Pongamia* Flowers

A lipid wax may be extracted, by means of ligroin, from the flowers of the poongaoil pongamia, *Pongamia glabra* Vent, which is indigenous from India and South China, to North Australia and the Fiji Islands. The flowers contain wax, oil, and a small amount of colorless crystalline substance (m. 212°C), which is known as *pongamin*. Murti and Seshadri[196a] state that the aliphatic waxy portion of the extractive is comprised of

esters derived from C_{24}–C_{34} alcoholic and C_{24}–C_{30} acids, and about 12 per cent of hydrocarbons, C_{27}–C_{33}.

PART IV: WAXES FROM MICROORGANISMS

The waxes derived from microorganisms include waxy material found in the soil, waxy material resulting from the putrefaction of animal substances, and waxes associated with bacilli, notably the tubercle bacilli of the human, bovian, and avian types.

Agricere Wax

The name *agricere* was given to a waxy substance found in the soil by Greig-Smith[90b]. The soil particles are covered with a waxy layer in nature; the waxy material is partially saponifiable. Schreiner and Lathrop[244] found that the wax layer consisted largely of *dihydroxystearic acid*, and that this acid could be found in one-third of the soils examined. More than half of the poor soils contained it, but few of the good soils. [Generally accompanied by xanthin and hypoxanthin they considered harmful to plants.]

Dihydroxystearic acid was found in soils under long cultivation, in virgin soils, and soils under the sod. It is likely to be encountered in soil work anywhere. Greig-Smith[90b] associated agricere with thermolabil bacteriotoxins which it can harbor. The toxins retard plant growth, but are destroyed by sunlight and heat. This investigator states that a good distribution of agricere is favorable to the soil, since extraction of the wax leads to a higher production of toxins, as solvent extraction experiments have shown.

Adipocere Wax

Braconnot in 1811 isolated a waxy material from mushrooms, which he termed *adipocire*. *Ergosterol* is found in such lower forms as brown algae, slime fungi, lichens, etc., and Deuel, Jr.[70a] postulates that the adipocere of Braconnot might well have been ergosterol.

The name "adipocere" is given to the waxy substance which forms in diseased human tissues. Abundant deposition of fat in the various tissues favors its formation. Adipocere wax is encountered in the decomposition of corpses in cemeteries. The putrefaction of vegetable substances by microorganisms produces a slight amount of adipocere, as do the food substances cottage cheese and lean meat.

The lipid, adipocere, consists of a mixture of esters of *palmitic acid*, *stearic acid*, and a smaller amount of *arachidic acid*. The acids are more or less combined with calcium as calcium soap. Traces of various minerals are present as impurities. *Hydroxystearic acids* in mono- or di-form are also found in human and pig adipocere. The alcohol obtained from the fat of

dermoid cysts termed "cetyl alcohol" is in reality *n-eicosyl alcohol* ($C_{20}H_{42}O$, m. 70°C). On oxidation it yields arachidic acid (m. 73°C).

The presence of *squalene* in dermoid cysts of the ovary is pathological, according to Dimter[68a]; the fat of these cysts can be separated by pressing into a solid fraction and a yellow, oily liquid. Squalene constitutes 15.9 per cent of the total unsaponifiable residue, or 4 per cent of the fat. From the caked wax-like portion (m. 87°C) of the residue it is possible to obtain by recrystallization from acetone and acetylation about 9 per cent of *docosanol*, $C_{22}H_{46}O$. *Carnaubyl alcohol* is thought to be a constituent. *Tetracosyl alcohol* is present in large amount. The absence of aldehydes, ketones, and hydrocarbons has been noted.

Bacillary Waxes

Human Tubercle Bacillus Wax. Human tubercle bacilli, and those of the bovian and avian types, contain lipoids which are of a wax, fat, and phosphatide composition. It has been shown that the acid-fast *Mycobacterium tuberculosis*, var. *hominis*, and related types, are encased with a lipide wax of high molecular weight constituents, thus making the capsulated bacillus very resistant to adsorption, penetration, and destruction, except by means of high heat. The wax coating of the bacillus is a relatively thick, impervious shell as revealed by the electron microscope.

In the early investigations of the constituents of the lipoids and of the lipide wax in particular, Kresling[141] extracted the dried mass of human tubercle bacillis with chloroform. Bullock and Macleod[42] in 1903 used Arenson's mixture, i.e., a mixture of alcohol and ether acidified with 1 per cent of hydrochloric acid, for extracting the lipides, and saponified the extract with sodium alcoholate. The residue which escaped saponification and which was fat free contained high molecular weight wax esters and some phosphatide. Fontes[81] in 1910 made his extractions in a Soxhlet apparatus using successively xylene, 95 per cent ethanol, ether, and chloroform.

In 1927 Anderson[3] extracted the lipides from moist, living tubercle bacilli with a mixture of ethanol and ether, followed by chloroform, in which the wax constituents are quite soluble. Over 2000 cultures were used, each containing about 2 grams of bacteria on a dry basis. The chloroform-soluble wax amounted to 427 grams. Anderson and co-workers, according to Lewkowitsch[157], purified the crude wax (m. 50–51°C) by precipitation from ether and toluene by methanol. This treatment yielded a white amorphous powder (m. 200–205°C) which they designated as "purified wax." The wax in the mother liquor they termed "soft wax." According to Anderson[3] the white powder upon hydrolysis yields 71 per cent of ether-soluble and nearly 40 per cent of water-soluble constituents. Approximately 56 per cent of the total wax consists of a snow-white powder, possessing both acid and alcohol

properties, which is designated as "unsaponifiable wax." The true fatty acids present were found to be *cerotic*; a eutectic mixture of *palmitic* and *stearic*; *oleic*; and a liquid-saturated fatty acid, namely *phthioic acid*. Several additional fatty acids of a branched-chain type were found by later investigators. The water-soluble constituents consist of glycerophosphoric acid, a mixture of reducing sugars that give pentose reactions, and some N-containing compound.

In a paper delivered to the National Academy of Sciences in 1929 Anderson[4a] postulated that the biological activity of the lipoids of tubercle bacilli was due to *phthioic acid*, a *d*-rotatory fatty acid of the formula $C_{26}H_{52}O_2$. To isolate phthioic acid the mixed acids obtained by hydrolysis of the phosphatide were converted to lead (Pb) soaps which are extracted with ether. The ether-soluble Pb soaps which contain oleic and phthioic acids are separated; catalytic reduction converts oleic acid to stearic acid, the Pb soap of which is insoluble in ether. Decomposition of the Pb salt of phthioic acid with dilute HCl yields free *phthioic acid*[4].

In the light of our knowledge of latterly investigations, supported by the National Tuberculosis Association, and those made by others both in the United States and abroad, the chemical composition of the lipide wax of human tubercle bacillus may be summed up as follows:

(a) Esters of high alcohols with normal saturated acids, *palmitic acid* and *stearic acid*, both of which are associated in the acetone-insoluble fraction of the alcohol-ether extract of the bacilli[321].

(b) *Cerotic acid* (*n*-hexacosanoic acid) isolated by Anderson[4] in 1929 and obtainable by distillation of the unsaponifiable wax as reported by Stodola and associates[253] in 1938.

(c) *Tuberculostearic acid*, $C_{19}H_{38}O_2$, which Spielman[253] in 1934 identified as *10-methyloctadecanoic acid*. It melts at 9–10°C. Prout and associates[220] from their study of optically active 10-methyloctadecanoic acids postulated that it is the L-10 acid (m. 12.8–13.4°C, $[\alpha]_D^{20}$ −0.05) and not the DL-10 acid (m. 25.4–26.1°C). Velick[300] confirmed the structure by measuring x-ray spacing values of the acid and its amides; the amides of both natural and synthetic acids proved identical.

(d) *Phthioic acid*, $C_{26}H_{52}O_2$, was isolated in a purified state by Anderson and Chargaff[5] in 1929. It melts at 20–21°C, and is biologically and optically active ($[\alpha]_D^{23}$ +12.78). As a result of many synthetical experiments bearing on the constitution of phthioic acid, Cason and Prout[47] have assigned it a structure with the methyl side-chain linkages in the 2, 3, 21 position which has a maximum molecular rotation of 49.5. The latter is

$$\begin{array}{l} CH_3\text{—}CH_2\cdot CH_2\cdot CH_2(CH_2)_{15}\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH \\ \qquad\quad | \qquad\qquad\qquad\qquad\qquad\quad | \quad | \\ \qquad\quad CH_3 \qquad\qquad\qquad\qquad\qquad CH_3\ CH_3 \end{array}$$

close to the 49.7 value actually observed for phthioic acid. All other trimethyltricosanoic acids would have a lower rotation.

(e) Branched-chain optical homologs of phthioic acid, namely *isotetracosanoic acid*, $C_{24}H_{48}O_2$ (m. 23–24°C); *isopentacosanoic acid*, $C_{25}H_{50}O_2$ (m. 17–18°C); *isoheptacosanoic acid*, $C_{27}H_{54}O_2$ (m. 20–21°C). All are fractionated from an acetone-soluble fat of an unidentified strain of tubercle bacillus residues which remained in the preparation of purified protein, known as PPD. According to Ginger and Anderson[88] the specific rotations of the C_{24}-, C_{25}-, C_{26}-, and C_{27}-acids are 5.17, 15.60, 12.78, and 17.11 respectively.

(f) *Mycocerosic acid*, $C_{30}H_{60}O_2$, is the name given to a levorotatory acid.

(g) Unsaturated branched-chain acid (m. 69–70°C) (of C_{26} series) with two terminal methyl groups was isolated by Polgar[208a].

(h) *Mycolic acid*, an hydroxy acid ether-soluble component of the less soluble wax fraction. This saturated hydroxy methoxy acid was reported by Anderson[157] in 1929, but its composition was not determined until 1938. The composition as given by Stodola, Lesuk and Anderson[263] was $C_{88}H_{172}O_4$ or $C_{88}H_{178}O_4$ (m. 54–58°C, $[\alpha]_D^{25\ Chf.}$ 1.8°). Anderson and Creighton[6] found the latter to be a mixture of optically active hydroxy acids which they termed α- and β-mycolic acids. The α acid (m. 55–56°C) when heated to 210–255°C under 1 mm pressure decomposes and a branched-chain pentacosanoic acid, $C_{25}H_{50}O_2$ (m. 78–79°C), distils off in a yield of 25 per cent. The β-acid (m. 71–73°C) decomposes at 280–295°C under 1 mm pressure, yielding 21 per cent of normal *tetracosanoic acid*. Precise structures of α- and β-mycolic acids still remain unknown.

The Stenhagens[260] at Upsala University, Sweden, have studied the mono- and multilayer behavior of such acids spread on 0.01*N* HCl and concluded that the acid (m. 78–79°C) is a mixture of closely related homologs such as *tetracosanoic* and *hexacosanoic acids*.

(i) *Oleic acid*.

(j) Dihydroxy monomethoxyl alcohol, known as *phthiocerol*, $C_{35}H_{72}O_3$[221]. This alcohol is found in all wax fractions; it may also have the formula $C_{36}H_{74}O_3$. Phthiocerol is optically active ($[\alpha]_D$ −4.8°), has a melting point of 73–74°C, and according to Stodola and associates[263], contains two hydroxyl and one methoxyl group. In the lipoids appreciable amounts of carbohydrates such as reducing sugars accompany the dihydroxy alcohols.

Emulsions prepared from ether or ether-methanol solutions of tubercle wax were found by Lucké to be best adapted for use as antigens, on the basis of clinical experimental data. These tubercle wax antigens appear to possess diagnostic and prognostic value in the serum diagnosis of tuberculosis.

Avian Tubercle Bacillus Wax. The dried bacterial mass of the avian type of tubercle bacillus contains 10.8 per cent of wax. The wax constitutes

10.8 per cent of the total lipoids, according to Reeves and Anderson[227]. After the wax has been purified and saponified the cleavage products were found to consist of fatty acids, unsaponifiable matter, and a water-soluble carbohydrate. The unsaponifiable consisted mainly of *d-eicosan-2-ol* (m. 62–63°C, $[\alpha]_D$ 6.79° in ether), with a small amount of *d-octadecan-2-ol* (m. 53–54°C, $[\alpha]_D$ 4.84° in chloroform). The water-soluble carbohydrate was identified as trehalose. Avian wax resembles timothy bacillus wax, both containing the previously mentioned constituents. The crude wax is a non-crystalline powder of a light-yellow color. It is soluble in chloroform, ether, benzene, toluene, ligroin, and ethyl acetate, but insoluble in acetone, ethanol, and methanol. It has a melting point of 53–54°C, iodine number 7.8, and saponification value 77, and is optically active ($[\alpha]_D$ in chloroform +25.6). The purified wax is a white crystalline granular powder, and has a melting point of 54–55°C and an iodine number of 4.8. It is optically active ($[\alpha]_D$ +38.6). The wax acids when separated in two fractions by extraction of the ligroin solution of the potassium salts with methanol had the approximate formulas $C_{38}H_{74}O_2$ and $C_{88}H_{174}O_2$. The C_{38}-acid melts at 69–70°C, is optically active ($[\alpha]_D$ 5.6°); molecular weight by titration is 500–520, iodine number 6.5. The C_{88}-acid melts at 60–61°C, is optically active ($[\alpha]_D$ 5.5°); molecular weight by titration is 1280–1300, iodine number 5.5. Both acids are acid-fast.

Bovine Tubercle Bacillus Wax. The chemistry of the lipides of the bovine type of tubercle bacillus, *M. tuberculosis*, var. *bovis*, is much the same as that of the human bacillus. Anderson and Roberts[7] found certain differences in the phosphatide fraction which place the bovine product in an intermediate position between the corresponding fractions obtained from the human and avian strains. This difference is also reflected in the biological properties.

	Bovine	Avian	Human
Phosphatide, crude	1.53%	2.26%	6.54%
Acetone-soluble-fat	3.34	2.19	6.20
Chloroform-soluble-wax	8.52	10.79	11.03
Total lipoids	13.40	15.26	23.78
Dried bacterial residue	85.50	83.71	75.01

Cason and Anderson[46] examined the purified chloroform-soluble wax of the bovine type of tubercle bacillus and found it quite similar in composition to that of the human bacillus. The carbohydrate is a complex mixture of organic phosphorus acids and a phosphorus containing neutral polysaccharide which on hydrolysis yields inositol monophosphoric acid, mannose, inositol, and an unidentified reducing sugar. On saponification of the wax certain ether-alcohol insoluble active wax acids containing OH and OCH_3 groups with an average molecular weight of 1200 and 630 are obtained.

The chief component is *mycolic acid*. The soluble active wax acids yielded on fractionation *palmitic acid* and a *tetracosanoic acid*; a small amount of unsaturated acids; a branched-chain inactive acid, $C_{18}H_{36}O_2$, isomeric with stearic acid; and a mixture of *l*-acids having an average molecular weight of 430. *Palmitic acid* is the only common fat acid found among the ether-soluble constituents of the wax.

A dihydric monomethoxy alcohol of the formula $C_{35}H_{69}(OH)_3$ or $C_{36}H_{71}(OH)_2$, has been isolated from bovine tubercle bacillus wax[158]. The properties of this alcohol are identical to those of phthicerol isolated from human tubercle bacillus wax.

Tuberculoprotein is prepared by repeated ammonium sulfate precipitations of the culture filtrate of BCG strain of *M. tuberculosis*, var. *bovis*. The purified wax (*tuberculoprotein wax*), soluble in chloroform, can be recovered from a crude extract by two precipitations from ethyl ether with two volumes of cold methanol.

PART V: MISCELLANEOUS NATURAL WAXES

Lipide Waxy Substances in Brain Material

Cerebrosides of nervous tissue, kidney, liver, egg yolk, etc., have constituents which on hydrolysis yield C_{24}-carboxylic acids. The chief waxy acids of the cerebrosides are *isotetracosanoic*, *nervonic*, *cerebronic*, and *hydroxytetracosenoic acids*. The constituents of the cerebron (*phrenosine*) complex are optically active; for example, cerebron is of +7.6° rotatory power[124]. Pure cerebron prepared from cow's brain by ether extraction, on cleavage with sulfuric acid yields a nitrogen compound and *cerebronic acid* (m. 100–101°C, $[\alpha]_D^{30}$ +4.16); the latter was isolated by Kiawaga and Thierfelder[124], and confirmed by Brigl[36]. It is a white crystalline powder; crystals are wart-like or cauliflower-type. Cerebronic acid contains an asymmetric carbon atom in the α-position. Klenk[125] has shown this acid to be α-hydroxylignoceric acid, $CH_3(CH_2)_{21}CHOH \cdot COOH$.

Levene and West[154] have identified an acid in cerebroside material which is not normal and called it *isotetracosanoic acid*, indicating a side-chain methyl in a C_{24}-acid. On reduction this acid yielded isotetracosane, melting at 51–51.5°C, contrasted to 53°C for tetracosane. According to Brigl[36], cerebronic acid has a racemic modification (m. 97–100°C). On conversion it yields a tetracosanoic acid which melts sharply at 81°C.[155]

From the petrolic ether extract of brain, Klenk[125a, 126] was able by hydrolysis of the cerebrosides and fractionating the fatty acids to obtain an unsaturated acid related to cerebronic acid. He determined this to be an hydroxy acid, $C_{24}H_{46}O_3$ (m. 65°C, $[\alpha]_D^{20}$ +2.87), with the structure

$$Me(CH_2)_7\,CH{:}CH(CH_2)_{12}\,CH(OH)COOH$$

namely *15-16α-hydroxytetracosenoic acid*, with the double bond the same distance from the terminal Me as in oleic acid. Klenk[126] had isolated an unsaturated acid, $C_{24}H_{46}O_2$ (m. 40–41°C), which he had named *nervonic acid*. Its structure is $Me(CH_2)_7CH:CH(CH_2)_{13}COOH$. By catalytic hydrogenation nervonic acid was converted to *n-lignoceric acid* (m. 85°C), and the latter proved identical to the *tetracosanoic acid* prepared from beech tar or from pure behenic acid. There is evidently a whole group of C_{24}-acids present in the cerebrosides and phosphatides. Page and Rudy[203] had found that the fatty acids of cephalin from human brain gave 30 per cent of *stearic acid*, and 22 per cent of highly unsaturated C_{22}-acids inclusive of a small proportion of unsaturated C_{18}-acids. On hydrogenation the unsaturated C_{22}-acids yielded behenic acid.

Chibnall and associates[50] have shown that brain lipides contain at least three α-hydroxylated saturated acids in the form of *phrenosins*. The acids are *α-hydroxy-n-docosanoic*, *α-hydroxy-n-tetracosanoic*, and *α-hydroxy-n-hexacosanoic acids*.

Klenk and Schumann[127] in their investigation of the unsaturated acids in brain cerebrosides precipitated and separated the fraction of unsaturated hydroxy acids as magnesium salts, and distilled the methyl esters of the remaining nervonic acid fraction *in vacuo*. A hexacosanoic acid was isolated from a methyl ester fraction distilling at about 173°C. The free acid crystallized from acetone in bright scales of 45–45.5°C melting point.

The cerebrosides are a distinctive group of conjugate lipids which contains a nitrogenous base, namely sphingosine, the aforesaid fatty acids of the C_{24} series, and a molecule of carbohydrate, which may be either galactose or glucose.

Wax of Human Blood Serum

By chromatographic adsorption methods Schulze[247] of the University Medical Clinic, Göttingen, Germany, was able to separate quantitatively human serum lipides into (a) phosphatides, (b) cholesterol esters, (c) free fatty acids, (d) neutral fats, free cholesterol, hydrocarbons, waxes and an unknown material. There is only a minute amount of the wax constituent.

Ear Wax

The lipides in the wax of the external auditory meatus are secreted by the sebaceous glands. The presence of triglycerides, cholesterol esters, plasmal, and some phospholipides in the glands have been demonstrated by Montagna[193], also the presence of proteins and pigment in the wax. McBeth and Warth[184a] have determined the softening and melting points by employing the Fisher-Johns method of determination. The wax softened at 51°C, with a constituent decomposing at 210°C (*Plasmalogen*, which is an acetal phos-

phatide, becomes soft at 50°C and decomposes above 150°C. C_{15}–C_{18} *triglycerides* also melt at 51°C but decompose at a higher temperature.) The only cholesteryl ester which melts at about 220°C, where the bulk of the ear wax melts, is *cholesteryl diadipate*. At 210°C the wax changed from yellow to red in color, characteristic of certain *carotenoids*. At 270°C the wax as a whole decomposed.

Wax Gland of Duck

The wax gland of the duck has about one-third of straight-chain fatty acids and two-thirds branched-chain acids. About 36 per cent of the acids are steam-volatile branched-chain acids of molar weights between C_7 and C_{10} which are optically active. Fractions of high molecular weight acids also contained considerable amounts of optically active branched-chain acids (between C_{10} and C_{18}).

References

1. Ahmad, N., and Sen, D. L., *Tech. Bull.*, **18B**, 6 pp. (1933).
2. Alcocer, G., and Sanders, J. M., *Anales inst. med. nacional, Mexico*, **2**, 155–162 (1910); [*Chem. Abstracts*, **6**, 432 (1912)].
3. Anderson, Rudolph J., *J. Biol. Chem.*, **74**, 525–535 (1927).
4. ——, *ibid.*, **83**, 169–175, 505–522 (1929).
4a. ——, *Proc. Natl. Acad.*, **15**, 628–633 (1929).
5. ——, and Chargaff, E., *J. Biol. Chem.*, **84**, 703–717 (1929); **85**, 77–88, 327–349, 351–354 (1929).
6. ——, and Creighton, M. M., *J. Biol. Chem.*, **129**, 57–63 (1939).
7. ——, and Roberts, E. G., *J. Biol. Chem.*, **85**, 529–538 (1930).
8. Anon., *Oil, Paint & Drug Reptr.*, **92**, No. 19, 17 (1917).
9. Anon., *Bull. Imp. Inst.*, **29**, 40–41 (1931).
10. Anon., *Revisto Commercitalo-brasil*, **12**, 33 (1929).
11. Anon., *Bull. Imp. Inst.*, **15**, 182–184 (1917).
12. Anon., *Chemurgic Digest*, **9**, [7], 9, (1950).
13. Aswath Narain Rao, K., and Gupta, G. N., *Proc. 10th Ann. Convention Sugar Tech. Assn., India*, Pt. 2, 79–82 (1941); [*Chem. Abstracts*, **37**, 5268 (1943)].
14. Avequin, M., "The Waxy Matter of Sugarcane," *Ann. Chim. phys.* (2), **75**, 218–222 (1840); *Ann.*, **37**, 170–173 (1841).
15. Ayres, Jr., E. E., *Textile World J.*, **51**, No. 20, 49–53 (1916).
16. Baer, E., and Fischer, H. O. L., *J. Biol. Chem.*, **140**, 397–410 (1941).
17. Baker, R. T., and Smith, H. G., *Proc. Roy. Soc., Tasmania*, 139–207 (Apr., 1913).
18. Balch, R. T., and Broeg, C. B. (Bur. Agr. & Ind. Chem. Research), Administration, U. S. Dept. Agriculture, Houma, La.), Agr. Chem. Research Div. Contribution No. 131 (1942).
19. Bardorf, C. F., *Can. Chem. Mat.*, **11**, 231–234 (1927).
20. Barenthcr, A., *Chem. Umschau Gebicte Fette, Öle, Wachse u. Harze*, **30**, 117 (1923).
20a. Barnes, C. S., *et al., Australian J. Applied Sci.*, **3**, 88–99 (1952).
20b. Bellamy, L. J., and Doree, C., *J. Chem. Soc.*, **1941**, 172–176.
21. Baughman, W. F., *et al., J. Am. Chem. Soc.*, **43**, 199–204 (1921).

21a. Becker, Max, *Biochem. Z.*, **239**, 235–242 (1931).
21b. Bennett, H., *et al.*, *Colonial Plant and Animal Products* (*Brit.*), **2**, 196–220 (1951) [*Chem. Abstracts*, **46**, 9327 (1952)].
22. Berg, R., *Chem. Ztg.*, **31**, 337–339 (1907).
23. ——, *ibid.*, **32**, 777–780 (1908).
24. ——, *ibid.*, **38**, 1162–3 (1914).
24a. Bergmann, W., *Textile Research*, **8**, 221–225, 399–405 (1938); **9**, 175–182 (1939).
25. Bertram, S. H., *J. Am. Oil Chem. Soc.*, **26**, 454–456 (1949).
26. Bessey, C. E., "Botany for High Schools and Colleges," 7th Ed. Revised, p. 93, New York, Henry Holt & Co., 1905.
27. Betrabet, M. V., and Chakravati, G. C., *J. Indian Inst. Sci.*, **16A**, 41–53 (1933).
28. Bianchi, A., and Malatesta, G., *Ann. chim. appl.*, **1**, 297–302 (1914).
29. Binaghi, R., and Falqui, P., *Ann. chim. appl.*, **15**, 386–396 (1925).
29a. Bishop, C. T., *et al.*, *Pulp Paper Mag. Can.*, **51**, No. 1, 90–92 (1950).
30. Bisson, C. S., and Dye, W. B., U.S. Patent 2,037,111 (1936).
30a. ——, Vansell, G. H., and Dye, W. B., *U. S. Dept. Agr. Tech., Bull.* **716**, 24 pp. (1940).
30b. Blair, E. H., *et al.*, *Ind. Eng. Chem.*, **45**, 1104–1106 (1953).
30c. Blount, B. K., *J. Chem. Soc.*, **1935**, 391–393.
30d. ——, *ibid.*, **1936**, 1241–1242.
31. Bohrisch, P., *Pharm. Centrh.*, **48**, 929–934 (1908).
32. Bolley, D. S., and McCormack, R. H., *Am. Oil Chem. Soc., Paper* 17: "Utilization of the Seed of the Chinese Tallow Tree," Fall Meeting, 1949.
33. Bolton, E. R., and Hewer, D. G., *Analyst*, **42**, 33–45 (1917).
34. Bontoux, E., *Soc. Chem. Ind.*, **28**, 429 (1909).
35. Bougault, J., and Bourdier, L., *J. pharm. chim.* [6], **29**, 561–573; *ibid.*, **30**, 10–16 (1909); *Compt. rend.*, **147**, 1311–1313 (1909).
36. Brigl, Percy, *Z. physiol. Chem.*, **95**, 161–194 (1915).
37. "British Pharmacopoeia," London, Publ. by General Council of Medical Education and Registration.
38. Broeg, C. B., and Balch, R. T., U.S. Patent 2,449,107 (1948).
39. Buchner, G., v., *Z. öffent Chem.*, **17**, 311 (1911).
40. ——, *Chem. Ztg.*, **31**, 570 (1907).
41. ——, *ibid.*, **42**, 373–374 (1918).
42. Bullock, W., and Macleod, J. J. R., *J. Hygiene*, **4**, 7 (1904).
43. Bunger, W. B., and Kummerow, F. A., *J. Am. Oil Chemists' Soc.*, **28**, 121–123 (1951).
44. Bunker, R. U., U.S. Patent 1,309,909 (1919).
45. Carleton, R. K., and Nealy, W. A., *Rept. New England Assoc. Chem. Teachers*, **43**, 84–88 (1942).
45a. Carter, C. L., *J. Soc. Chem. Ind.*, **47**, 26–30T (1928).
46. Cason, J., and Anderson, R. J., *J. Biol. Chem.*, **85**, 527–541, 549–551 (1930).
47. ——, and Prout, F. S., *J. Am. Chem. Soc.*, **70**, 879–880 (1948).
48. Chibnall, A. C., and Piper, S. H., *et al.*, *Biochem. J.*, **25**, 2095 (1931).
49. ——, *et al.*, *Biochem. J.*, **28**, 313–325 (1934).
50. ——, ——, *ibid.*, **30**, 100–114 (1936).
51. ——, ——, *ibid.*, **31**, 1981–1986 (1937).
52. Chilikin, M. M., and Kamolova, L. D., *Khim. Referat. Zhur.*, (*U.S.S.R.*), **1939**, No. 6, 117; [*Chem. Abstracts*, **34**, 3939 (1940)].
53. Chuit, P., and Hausser, *J. Helv. Chim. Acta*, **12**, 463–493 (1929).
54. Clark, I. L., *et al.*, *J. Am. Chem. Soc.*, **69**, 3142 (1947).

55. Clotofski, E., *et al.*, *Ber.*, **74B**, 299–307 (1941).
56. ——, and Herr, W., *Ber.*, **75B**, 237–243 (1942); *Chem. Zentr.*, **1942**, **1**, 2148.
57. Collins, F. J. E., *J. Soc. Chem. Ind.*, **54**, 33–35T (1935).
58. Conrad, C. M., and Neely, J. W., *J. Agr. Research* **66**, 307–312 (1943).
59. Cooke, G. B., *Wallerstein Labs. Commun.*, **VII**, 20, 27–32 (April 1944).
60. Cortese, D., *Atti II congresso naz. chim. pura applicata*, **1926**, 1347–1352.
60a. Cousins, E. R., *et al.*, *J. Am. Oil Chem. Soc.*, **30**, 9–14 (1953).
61. Cox, W., and Reid, E. E., *J. Am. Chem. Soc.*, **54**, 220 (1932).
62. Cross, C. F., and Russell, R., British Patent 8,268 (1908).
63. D'Ambrosio, A., *Ann. chim. applicata*, **16**, 443–451 (1926); *Chem. Abstracts*, **21**, 893 (1927).
64. Damoy, G., *J. Pharm. chim.*, **29**, 148–158, 225–236 (1924).
64a. Daniel, D., Lederer, E., and Velluz, L., *Bull. soc. chim. biol.*, **27**, 211–218 (1945).
65. Darmstädter, F., and Lifschütz, M., *Ber.*, **30**, 2890 (1897).
65a. Daugherty, P. M., *et al.*, *Engineering Experiment Station of the Georgia Institute of Technology*, **25**, No. 12, 1–55, Bull. No. 16 (1953).
66. De, C. C. (Nakum, Ranchi, Bihar, India), *Indian Lac Research Inst. Research Note*, No. 34, 3 pp. (1945); [cf. *Chem. Abstracts*, **42**, 5239 (1948)].
66a. De Navarre, M. G., "Waxes, Bulletin No. 10," Am. Perfumer and Essntial Oil Review (1941).
67. Dickinson, T. A., *J. Pharm.*, **91**, 808–809 (1919).
67a. Dieterich, K., *Pharm. Zentralhalle*, **52**, 1019–1027 (1912).
68. Dieterle, H., *Arch. Pharm.*, **361**, 89–98 (1923); *Chem. Zentr.*, **1923**, III, 938.
68a. Dimter, A., *Z. physiol. Chem.*, **270**, 247–265 (1941).
69. Drake, B. L., and Jacobsen, R. P., *J. Am. Chem. Soc.*, **57**, 1570–1574 (1935).
69a. Drake, N. L., Carhart, H. W., and Mozingo, R., *J. Am. Chem. Soc.*, **63**, 617–620 (1941).
70. Drekter, I. J., and Conrad, L. I. (Am. Cholesterol Products Co.), U.S. Patent 2,302,679 (1942).
70a. Deuel, Jr., H. J., "The Lipids," p. 321, New York, Interscience Publishers, Inc., 1951.
71. Dupont, G., and Guillemonat, U.S. Patent 2,571,221 (1951).
72. Dutch Patent 29,780, N. V. Olieraffinaderij "Zuilen," 1933; [cf. *Chem. Abstracts*, **27**, 4631, (1933)].
72a. Dutt, S., and Prakash, I., *Indian Soap J.*, **15**, 77–82 (1949).
73. "Encyclopaedia Brittanica," 14th Ed. Rev. ed., New York. Encyclopaedia Brittanica, Inc., 1929.
74. Evers, N., and Foster, H. J., *Pharm. J.*, **105**, 100 (1920); *Chemist and Druggist*, **93**, 1066 (1920).
75. Faber, H. A., and Howard, P. F. (Chlorine Institute, N. Y.), *Water & Sewage Works*, **93**, 467–473 (1946).
76. Farcy, L., *J. pharm. chim.*, **22**, 174–175 (1920).
77. Fargher, R. G., and Probert, M. E., *J. Textile Inst.*, **14**, 49–65T (1923).
78. Feldstein, L., *Ind. Eng. Chem.*, **4**, 498 (1912).
78a. Feurt, S. D., and Fox, L. E., *Science*, **117**, 600 (1952).
78b. Fierz-David, H. E., and Ulrich, C., *Experientia*, **1**, 160 (1945).
79. Findley, T. W., and Brown, J. B., *J. Am. Oil Chemists' Soc.*, **30**, 291–298 (1953).
80. Flaschenträger, P., and Halle, F., *Z. physiol. Chem.*, **190**, 120–140 (1930).
81. Fontes, A., *Centr. Bakt. Parasitenk (Rio de Janeiro)*, **1**, Abt. **49**, 317–321 (1911).
82. Fraps, C. S., and Rather, J. R., *Ind. Eng. Chem.*, **2**, 454 (1910).
83. Frerichs, G., *Apoth. Ztg.*, **31**, 223 (1916); *Chem. Zentr.*, **II**, 283 (1916).

83a. Fujita, A., and Yoshikawa, T., *J. Pharm. Soc. Japan*, **71**, 913–916 (1951).
84. Gascard, A., *Compt. rend.*, **159**, 258–260 (1914).
85. ——, *ibid.*, **170**, 1326–1328 (1920).
86. Gascard, A., and Damoy, G., *Compt. rend.*, **117**, 1222–4, 1442–3 (1923).
87. Gibson, W. H., *Trans. Inst. Chem. Eng.*, Advance copy 3–6 (March 5–6, 1931).
88. Ginger, G., and Anderson, R. J., *J. Biol. Chem.*, **156**, 443–454 (1944); **157**, 203–211 (1945).
88a. Gomes, Pimentel, Ministerio agr., *Service documentacao S.D.A.*, **220**, 3–6 (1945).
89. Gonzalez-Trigo, G., *Anales bromatol. (Madrid)*, **2**, 31–46 (1950).
89a. Gottfried, S., and Ulzer, F., *Chem. Umschau Fette, Öle, Wachse u. Harze*, **33**, 141–145 (1926).
90. Green, T. G., *et al.*, *J. Chem. Soc.*, **1936**, 1750–1755.
90a. Greene, R. A., and Foster, E. O., *Bot. Gaz.*, **94**, 826–828 (1933).
90b. Greig-Smith, Sydney, *Centr. Parasitenk*, **II** Abt., **34**, 224–226 (1912).
91. Greshoff, M., and Sack, J., *Rec. trav. Chim.*, **20**, 65 (1901).
92. Grimme, C., *Chem. Rev. Fett-Harz-Ind.*, **17**, 233–237 (1910).
93. Grodman, B., *Chem. Analyst*, **25**, 81 (1936).
94. Gupta, M. P., and Dutt, S., *Proc. Natl. Acad. Sci. India*, **8**, 49–52 (1938).
94a. Gupta, S. S., and Meara, M. L., *J. Chem. Soc.*, **1950**, 1337–1342.
95. Haar, A. W., Van der, *Rec. trav. chim.*, **43**, 542–545 (1924).
95a. Hackman, R. H., *Arch. Biochem. Biophys.*, **33**, 150–154 (1951).
96. Harding, T. S., *Am. J. Pharm.*, **119**, 429–431 (1947).
96a. Hardwick, P. J., and Laws, E. Q. (Govt. Lab. Strand, London), *Analyst*, **76**, 662–664 (1951).
97. Hare, R. F., and Bjerregaard, A. P., *Ind. Eng. Chem.*, **2**, 203–205 (1910).
98. Hata, C., *J. Chem. Soc. Japan*, **58**, 1188–1192 (1937); [*Chem. Abstracts*, **32**, 3994 (1938)].
98a. Hata, T., and Kunisaki, T., *J. Chem. Soc. Japan*, **61**, 1288–1291 (1940).
98b. Hatt, H. H., *et al.*, *Proc. Queensland Soc. Sugar Cane Tecnol.*, **17**, 61–81 (1950).
99. Heiduschka, A., and Gareis, M., *J. prakt. Chem.*, **99**, 293–311 (1919).
99a. ——, and Nier, E., *J. prakt. Chem.*, **149**, 98–106 (1937).
100. ——, and Vogel, F. M., *Pharm Zentralhalle*, **53**, 1087–1088 (1913).
100a. Helfenberg, K. D., *Chem. Ztg.*, **31**, 987–988 (1907).
101. Henriques, V., *Ber.*, **30**, 1415 (1897).
102. Herbert, A., and Heim, F., *Bull. Office Colonial* (Madagascar), **8**, 86, 96–101 (1915); [*J. Soc. Chem. Ind.*, **34**, 1061 (1915)].
103. Herbig, W., "Die Öle u. Fette in der Textile Industrie," Vol. 3, Monograph Series, Stuttgart, Wissenschafliche Verlagegesellschaft m.b. H., 1923.
103a. Hewett, C. L., Organon Laboratories Ltd., British Patent 646,227 (1951).
104. Higgins, S. H., *J. Soc. Chem.*, **33**, 902–905 (1914).
105. Hilditch, T. P., "Industrial Chemistry of Fats and Waxes," New York, D. Van Nostrand Co., Inc., 1927.
106. ——, and Lovern, J. A., *J. Soc. Chem. Ind.*, **47**, 105T (1928); **48**, 359–365T (1929).
107. Hirschler, H. E., and Amon, S., *Ind. Eng. Chem.*, **39**, 1585 (1947).
108. Hoffmeister, C., *Ber.*, **36**, 1047–1054 (1903).
109. Holde, D., and Bleyberg, W., Metallbörse, **20**, 1855–6 (1930).
110. Horn, D. H. S., and Houghen, F. W., *Chemistry & Industry*, **1951**, 670.
110a. ——, *et al.*, *ibid*, **1953**, 106.
110b. Hugh, R. D., unpublished thesis, Tempe, Arizona (1951).
111. Huminski, W., *Roczniktk Chem.*, **15**, 53–56 (1935); [*Chem. Abstracts*, **29**, 4613 (1935)].

111a. Huzzi, K., and Osumi, S., *J. Pharm. Soc., Japan*, **60**, 291–300 (1940); [*Chem. Abstracts*, **34**, 7293 (1940).
112. Iachan, A., and Gottlieb, O., *Rev. quim. ind.*, **19**, No. 215, 16–17 (1950).
112a. Ikeda, I. H. (Univ. Tokyo), *J. Chem. Soc. Japan, Pure Chem., Sect. 72*, **1951**, 245–246.
113. Ikuta, H., *J. Soc. Chem. Ind., Japan*, **36**, Suppl. binding, 377–379, 444–447 (1933).
114. ——, *Chem. Umschaugebiete Fette, Öle, Wachse u. Harze*, **38**, 7–10 (1931).
115. Industrial Reference Service, U. S. Dept. of Commerce, **5**, part 12, No. 16 (August 1947).
115a. Inoue, S., *J. Soc. Chem. Ind., Japan*, **40**, Suppl. binding 23–24 (1937).
116. Isely, C. C., *Food Ind.*, **21**, 53 (1940).
116a. Ishiwata, Y., Japanese Patent 4533 (1951); cf. *Chem. Abstracts*, **47**, 3012 (1953).
117. Ivanovszky, L., *Oil Colour Trades J.*, (Dec. 20, 1940).
118. Jacini, G., *Gazz., chim. ital, mazie*, **77**, 247–251 (1947).
119. Jacobsen, J. J., *Cotton Oil Press*, **6**, No. 1, 43–44 (1922).
119a. Jamieson, G. S., "Vegetable Fats and Oils," 2d. Ed., New York, Reinhold Publishing Corp., 1943.
119b. Jensen, W. (Åbo Akad., Turku, Finland), *Paper and Timber* (*Finland*), **32**, 261–266 (1950) (in English).
119c. Jermstad, A., *Pharm. Acta Helv.*, **8**, 69–70 (1933).
120. Kariyone, T., *et al.* (Univ. Kyoto), *J. Pharm. Soc. Japan*, **72**, 5–13 (1952).
120a. Kawakami, Y., *J. Nippon Oil Technol. Soc.*, **2**, No. 1, 33–41 (1949).
121. Kebler, L. F., *Am. J. Pharm.*, **1893**, 585.
122. ——, *ibid.*, **1896**, 7; **1897**, 104.
123. Kelsey, H. D., and Dayton, W. A., "Standardized Plant Names," 2d Ed., Harrisburg, Pa., J. Horace McFarland Company, 1942.
124. Kiawaga, F., and Thierfelder, H., *Z. physiol. Chem.*, **49**, 286–292 (1907).
125. Klenk, E., *Z. physiol. Chem.*, **157**, 283–290, 291–298 (1926); **145**, 244–260 (1925).
125a. ——, *ibid.*, **174**, 214–232 (1928).
126. ——, *ibid.*, **166**, 268–286, 287–293 (1927).
127. ——, and Schumann, E., *Z. physiol. Chem.*, **272**, 177–188 (1924).
128. Knaggs, N. S., "Adventures in Man's First Plastic," New York, Reinhold Publishing Corporation, 1947.
129. Knecht, E., *Textile Inst. J.*, **2**, 22–29 (1912); cf. *J. Soc. Chem. Ind.*, **30**, 1007 (1912).
130. ——, and Allan, J., *J. Soc. Dyers Colourists*, **27**, 142–146 (1911).
131. ——, and Hall, W., *J. Soc. Dyers Colourists*, **34**, 220–227 (1918).
132. ——, and Streat, G. H., *J. Soc. Dyers Colourists*, **39**, 73–77 (1923).
133. Knol, N. V., *J. Am. Oil Chem. Soc.*, **31**, 59–62 (1953).
134. Kono, M., *J. Agr. Chem. Soc. Japan*, **8**, 1150–1160 (1932).
134a. ——, *ibid.* **9**, 1276–1283 (1933).
135. ——, and Maruyama, R., *J. Agr. Chem. Soc. Japan*, **10**, 1228–1235 (1934).
136. ——, and ——, *ibid.*, **11**, 647–658 (1935).
137. ——, and ——, *ibid.*, **12**, 512–520, 523–530 (1936).
138. ——, and ——, *ibid.*, **14**, 697–701; **15**, 178–181 (1939); [*Chem. Abstracts*, **33**, 2594, 6239, 8317 (1939)].
139. Koonce, S. D., and Brown, J. B., *Oil & Soap*, **21**, 231–234 (1944).
140. Koyama, R., *J. Chem. Soc. Japan*, **54**, 1233–1237 (1933).
140a. ——, *ibid.*, **55**, 348–352, 802–808 (1934).

140b. ——, *ibid.*, **56**, 365–372 (1935); [*Chem. Abstracts*, **29**, 4613 (1935)].
141. Kresling, K. I., *Cent. Bakt.*, **1**, Abt., 30, 897 (1901).
141a. ——, *Z. physiol. Chem.*, **32**, 355 (1901); **72**, 455 (1911).
142. Kügler, *Arch. Pharm.*, **22**, 217 (1884); *Ber.*, **17**, 213 (1884).
143. Kummerow, F. A., *et al.*, *Am. Miller and Processor*, **1947**, 94–95, 143, [*Oil & Soap*, **23**, 167–170, 273–275 (1946)].
144. Kurth, E. F., *et al.*, *Timberman*, **49**, 130–131 (1948).
145. ——, and Kiefer, H. J., *Tappi*, **33**, 183–186 (1950).
145a. ——, and Hubbard, J. K., *Ind. Eng. Chem.*, **43**, 896–900 (1951).
146. Kurtz, Jr., E. B., *Plant Physiol.*, **25**, 269–278 (1950).
147. Kuwata, T., *J. Am. Chem. Soc.*, **60**, 559–560 (1938).
148. ——, and Ishii, Y., *J. Soc. Chem. Ind., Japan*, **39**, Suppl. binding, 317–319, 358–359 (1936); [*Chem. Abstracts*, **31**, 1235 (1937)].
149. ——, and Kutuno, M., *J. Soc. Chem. Ind., Japan*, **41**, Suppl. binding, 227–228 (1938); [*Chem. Abstracts* **32**, 9536 (1938)].
150. Lach, B., *Seifensieder Ztg.*, **42**, 929–931, 9501 (1915).
150a. Lederer, E., and Kiun, T. P., *Bull. soc. chim. biol.*, **27**, 419–424 (1945).
150b. Lee, J. A., *Food Eng.*, **24**, No. 12, 98 (1952).
151. Lecs, P. M., and Ibarra, H. P. Y., *Rev. asoc. ing. agron.*, **15**, 9–20 (1943).
152. Legg, V. H., and Wheeler, R. V., *J. Chem. Soc.*, **1929**, 2444–9.
153. Lepierre, C., and Carvalho, A., *Chimie Industrie*, **29**, 1087 (1933).
154. Levene, P. A., and West, C. J., *J. Biol. Chem.*, **15**, 193–195 (1913); **18**, 477–480 (1914).
155. ——, and ——, *ibid.*, **26**, 115–120 (1916).
156. Lewkowitsch, J., *Analyst*, **33**, 313–315 (1908).
157. ——, "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed., Vol. II, p. 927, London, Macmillan & Co., Ltd., 1915.
158. ——, p. 900.
158a. ——, *ibid.*, p. 108.
159. ——, *ibid.*, 6th Ed., Vol. II, p. 945 (1922).
160. Leys, A., *Ann. chim. anal.* (*Paris*), **17**, 334–342; *Mat. grasses*, **5**, 2887–8, 2913–4, 2951; [*J. pharm. chim.* **5**, 577–588 (1913)].
161. ——, *J. pharm. Chim.* [8] **1**, 417–424 (1925).
162. Liebermann, C., *Ber.*, **28**, 1979 (1885).
163. Lipp, A., and Casimer, E., *J. prakt. Chem.*, **99**, 256–268 (1919).
164. ——, and Kovács, E., *J. prakt. Chem.*, **99**, 243–255 (1919).
165. ——, and Kuhn, E., *J. prakt. Chem.* **86**,, 184–189 (1913).
166. Lipson, M., *J. Council Sci. Ind. Research*, **13**, 273–277 (1940).
167. Louveau, G., *Rev. marques parfumerie et savonneris*, **1931**, No. 1–2; [*Chem. Abstracts*, **25**, 5306 (1931)].
167a. ——, *ibid.*, **9**, 531–533, 573–574, 622–623 (1931).
168. Lüdecke, C. (Milano, Italy), *Seifen-Öle-Fette-Wachse*, **74**, 111–113 (1948).
169. ——, *Fette u. Seifen*, **48**, 452–461 (1941).
170. Lower, E. S., *Mfg. Chemist, London*, **14**, 230 (August, 1943).
170a. ——, *Ind. parfum.*, **2**, 319–324 (1947).
171. Machado, A. A. de Souza. *Bol. ministerio agr.* (*Brazil*), **29**, No. 7, 17–20 (1940); [*Chem. Abstracts*, **35**, 6824 (1941)].
172. Marcelet, H., *Compt. rend.*, **204**, 1446 (1937).
173. Marcusson, J., and Skopnik, A. V., *Z. angew. Chemie*, **25**, 2577–2580 (1913).

174. ——, and Böttger, *Ber.*, **57B**, 633–635 (1924).
175. Markley, K. S., *J. Biol. Chem.*, **55**, 611–628 (1923); *J. Am. Chem. Soc.*, **46**, 150–160 (1924).
175a. Markley, K. S., *J. Am. Oil Chemists, Soc.*, **30**, 309–313 (1953).
176. ——, and Sando, C. E., *J. Biol. Chem.*, **105**, 643–653 (1934).
177. ——, Hendriks, S. B., and Sando, C. E., *J. Biol. Chem.*, **111**, 133–146 (1935).
178. ——, *et al.*, *J. Biol. Chem.*, **119**, 641–645 (1937).
178a. ——, ——, *ibid.*, **123**, 641–654 (1938).
178b. ——, ——, *ibid.*, **118**, 433–441 (1937).
179. Markwood, L. N., *Domestic Commerce*, **30**, 20 (1942).
179a. Marsel, C. J., *Chem. Ind.*, **66**, 216–218 (1950).
179b. Marsel, C. J., *et al.*, *Soap Sanit. Chemicals*, **28**, No. 11, 127, (1952).
180. Martin, G., "Animal, Vegetable Oils, Fats and Waxes," London, Crosby, Lockwood & Sons, 1920.
181. Marie, T., *Compt. rend.*, **1894**, 119, 428, 431.
181a. Marwedel, J., German Patent 735,791, 1943.
182. Masami, O., *Bull. Agr. Chem. Soc., Japan*, **4**, 123–125 (1928); [*Chem. Abstracts*, **24**, 3905 (1930)].
183. Matthes, H., and Heintz, W., *Arch. Pharm.*, **247**, 650–657 (1910).
184. Matthes, H., and Streicher, L., *Arch. Pharm.*, **251**, 438–452 (1914).
184a. McBeth,C., unpublished analytical determinations (1953).
185. McKay, A. F., *J. Org. Chem.*, **13**, 86–88 (1948).
186. McKinney, R. S., and Jamieson, G. S. (Bureau of Chemistry and Soils, Washington, D. C.), *Oil ; Soap*, **13**, 289–292 (1936).
187. McLoud, E. S., U.S. Patent, 2,456,641 (1948).
187a. Meier, Karl (Tech. Univ. Berlin), *Farbe u. Lack*, **57**, 437–439 (1951).
188. Meldrum, R., *Chem. News*, **111**, 37–39 (1915).
189. Meyer, H., and Eckert, A. (Lab. allg. anal. Chem. deut. tech. Hochschule Prag), *Monatsch.*, **31**, 1227 (1910).
190. ——, and Soyka, W. (*Univ. Prag.*), *Monatsch.*, **34**, 1159–1172 (1913).
190a. Mirov, N. T., *Chemurgic Digest*, **9** [7], 7–9 (1950).
190b. Mitra, C., and Siddiqui, S., *Current Sci. (India)*, **17**, 51 (1948).
190c. Mitsui, T., and Matsuda, J., *J. Agr. Chem. Soc. Japan*, **18**, 719–722 (1942).
191. Mitsui, T., *J. Agr. Chem. Soc., Japan*, **13**, 494–501 (1937); **14**, 342 (1938); **15**, 526 (1939); **16**, 144 (1940).
191a. Modi, P. K., and Khorana, M. L., *Indian J. Pharm.*, **14**, 61–63, 66 (1952).
192. Mollan, R. M., *Anais. assoc. quim. Brasil*, **2**, 75–76 (1943); [*Chem. Abstracts*, **38**, 1134 (1944)].
193. Montagna, W., *J. Morphol.*, **85**, 423–441 (1949).
193a. Monti, L., *Ann. chim. applicata*, **30**, 303–307 (1940).
194. Moore, C. W., *Proc. Chem. Soc.*, **26**, 85; [*J. Chem. Soc.*, **95**, 734–751 (1909)].
194a. Müller, Jorge, *Ind. farm. venezolana*, **2**, 20–35 (1946); *Rev. soc. venezolana quim.*, **3**, 8–13 (1946).
195. Murray, K. E., and Schoenfeld, R., *J. Am. Oil Chemists' Soc.*, **28**, 461–466 (1951).
195a. ——, and ——, *ibid.*, **29**, 416–420 (1952).
196. Murti, P. B. R., and Rao, N. V. S., *Proc. Indian Acad. Sci.*, **20A**: 163–168 (1944).
196a. ——, and Seshadri, T. R., *Proc. Indian Acad. Sci.*, **20A**, 266–273 (1944).
196b. ——, and ——, *ibid.*, **21A**, 8–18 (1945).
196c. ——, and ——, *ibid.*, **22A**, 289–292 (1945).
196d. Musgrave, O. C., *et al.*, *Journ. Chem. Soc.*, 4393–4397 (Nov. 1952).

197. Nabenhauer, F. B., and Anderson, R. J., *J. Am. Chem. Soc.*, **48**, 2972–2976 (1926).
197a. Nakamori, E., *J. Chem. Ind. Japan*, **22**, 318–319 (1919).
198. Nealy, W. A., *Western Canner & Packer*, **33**, No. 12, 22–23 (1941).
198a. Nealy, W. A., *Chemurgic Digest*, **2**, 14, 113–116 (1943).
199. Nishimura, M., and Nishimoto, Y., *J. Nippon Technol. Soc.*, **1**, No. 3, 39–45 (1948).
199a. Nobori, H., *J. Soc. Chem. Ind. Japan*, **44**, 1009–1011 (1941).
200. Nozoe, T., Japan Patents, 153,628; 153,629 (1942); [cf. *Chem. Abstracts*, **43**, 3219 (1949)].
201. N. V. Veenendaalache Sajet en Vijfschachtfabriek voorheen Wed. D. S. van Schuppen en Zoon, Dutch patent 58,771 (1947).
202. Olsson-Seffer, P., *Am. Rev. Tropical Agr.*, **1**, 108–111 (1911); [*Chem. Abstracts*, **5**, 2192 (1911)].
203. Page, I. H., and Rudy, H., *Z. physiol. Chem.*, **205**, 115–125 (1932).
204. Paula, R. D. de G., *Rev. alimentar* (*Rio de Janeiro*), **8**, 5–9 (1944).
205. Pegorari, Carle, *Pitture e varnici*, **2**, 401–402 (1946).
206. Pendse, G. P., and Dutt, S., *Bull. Acad. Sci. United Provinces, Agra Oudh, India*, **3**, 209–214 (1934); [*Chem. Abstracts*, **29**, 7577 (1935)].
207. Picard, C. W., and Seymour, D. E., *J. Soc. Chem. Ind.*, **64**, 304–305 (1945).
208. Pieraerts, J., *Mat. Grasses*, **14**, 5990–5992, 6020–6021 (1921).
208a. Polgar, N., *Biochem. J.*, **42**, 206–211 (1948).
209. Politzer, W., *Chemistry and Industry*, **1948**, 408–409.
210. Pollard, A., *et al.*, *Biochem. J.*, **25**, 2111–2122 (1931).
210a. Porter, A. B., U.S. Patent 2,499,877 (1950).
211. Potts, W. M., and Bolley, D. S., *Oil & Soap*, **23**, 316–318 (1916).
212. Power, F. B., and Browning, Jr., H., *J. Chem. Soc.*, **105**, 1829–1845 (1914).
213. ——, and ——, *Proc. Chem. Soc.*, **28**, 285; *J. Chem. Soc.*, **101**, 2411–2429 (1912).
214. ——, and Moore, C. W., *J. Chem. Soc.*, **97**, 1099 (1910); *Proc. Chem. Soc.*, **26**, 124 (1910).
215. ——, and Rogerson, H., *J. Am. Chem. Soc.*, **32**, 80 (1910).
216. ——, and Tutin, F., *Proc. Chem. Soc.*, **24**, 117–118 (1908).
217. Prandi, O., *Staz. sper. agrar. ital.*, **53**, 309–316 (1920).
218. Prophéte, H., *Compt. rend.*, **182**, 1559–1561 (1926).
219. ——, *Bull. coc. chim.*, **39**, 1600–1610 (1926).
220. Prout, F. S., *et al.*, *J. Am. Chem. Soc.*, **70**, 298–305 (1948).
221. Radcliffe, L. G., and Allan, J., *J. Soc. Chem. Ind.*, **27**, 227 (1908).
222. Rakshit, J. N., *Analyst*, **43**, 321–322 (1918).
223. Ramos, F., and Nascimento, R. C., *Rev. chim. ind. Rio de Janeiro*, **7**, 186 (138).
224. Rangaswami, S., and Sankarasubramian, S., *Current Sci.*, **15**, 316–317 (1946).
226. Raoul, W., *Ministerio trabalho ind. e com. Inst. nacl. tecnol.* (*Rio de Janeiro*), **1948**, 82 pp.
227. Reeves, R. E., and Anderson, R. J., *J. Am. Chem. Soc.*, **59**, 858–861 (1937).
228. Reichert, J. S., *et al.*, U.S. Patent 2,113,433 (1938).
229. Reyes, D. G., *Rev. quim. farm.*, (*Santiago, Chile*), **5**, 7–17 (1948).
230. Rhodes, F. H., and Swenson, O. J., U.S. Patent 2,431,634 (1947).
230a. Ribas, I., and Curbera, G. G., *Anales real soc. espan. fis. y quim*, **47B**, 713–714 (1951).
231. Rindl, M., *S. African J. Ind.*, **5**, 513–518 (1922).
231a. Riviére, G., and Pichard, G., *Compt. rend.*, **179**, 775–777 (1924).

232. Rogerson, H., (Welcome Chem. Research Lab., London), *Proc. Chem. Soc.*, **26**, 112 (1910).
233. Root, A. I., and Root, E. R., "The ABC and XYZ of Bee Culture," Medina, Ohio, The A. I. Root Co., 1940.
234. Root, H. H., "Beeswax," Brooklyn, N. Y., Chemical Publishing Co., Inc., 1951.
235. Russell, R. P., U.S. Patent 2,170,665 (1939).
236. Ruzicka, L., Rey, E., and Muhr, A. C., *Helv. Chim. Acta*, **27**, 472–489 (1944).
237. Ryan, H., *Sci. Proc. Royal Dublin Soc.*, **12**, 210 (1914).
238. Sabetay, S., *Ind. Perfum.*, **5**, 86 (1950).
238a. Sakurui, Z., *J. Pharm. Soc. Japan*, **53**, 579–580 (1933).
239. Sanders, J. M., *Proc. Chem. Soc.*, **27**, 250 (1911).
240. Sando, C. E., *J. Biol. Chem.*, **56**, 457–468 (1923).
241. Scalione, C. C., and Blakemore, H. S., *Ind. Eng. Chem.*, **8**, 411–413 (1916).
242. Schaal, R., *Ber.*, **40**, 4784–4788 (1907).
243. Schoeman, D. J., and Hawke, F., *J. S., African Chem. Ind.*, **1**, 5–13 (1948).
244. Schreiner, O., and Lathrop, E. C., *J. Franklin Inst.*, **172**, 142–151 (1911); *J. Am. Chem. Soc.*, **33**, 1412–1417 (1911).
245. Schmidt, W. J., *Z. wiss. Mikroscop*, **50**, 296–304 (1940).
245a. Schroger, A. W., *Ind. Eng. Chem.*, **19**, 409 (1927).
246. Schuette, H. A., and Baldinus, J. G., *J. Am. Oil Chemists' Soc.*, **26**, 530–532, 651–652 (1949).
246a. Schulz, F. N., and Becker, M., *Biochem. Z.*, **235**, 233–239 (1931).
247. Schulze, G., *Arch. exptl. Path. Pharmakol.*, **214**, 473–480 (1952).
247a. Schwarz, H. F., *Nat. History*, **53**, 414 (1944).
248. Scurti, F., and Tommasi, G. (Agr. Exp. Stat. Turin), *Gazz. chim. ital.*, **46**, 11, 159–168 (1916); [*Chem. Abstracts*, **11**, 1157 (1917)].
248a. ——, and, ——, *J. Soc. Chem. Ind.*, **32**, 572 (1913).
249. Shiina, S., *J. Soc. Chem., Ind. (Japan)*, **44**, 808–812 (1941).
250. ——, *ibid.*, **47**, 674–676 (1944); **49**, 18–20 (1946).
251. Shinosaki, Y., and Kubo, H., *J. Soc. Chem. Ind. (Japan)*, **37**, suppl. binding, 677–678 (1934).
252. Shriner, R. L., *et al.*, *J. Am. Chem. Soc.*, **49**, 5, 1290–1294 (1927).
252a. Singh, P., *J. Soc. Chem. Ind.*, **29**, 1435 (1911).
253. Smith, L. H., *J. Soc. Chem. Ind.*, **30**, 405 (1911).
254. Smith, H. W., and Campbell, S. G., British Patent 553,322 (1944).
255. Smith, W. R., and Wade, F. B., *J. Am. Chem. Soc.*, **25**, 629–632 (1903).
256. Smith, F. v. M. H. G., *J. Soc. Chem. Ind.*, **41**, 372 T (1922).
256a. Sörm, F., and Bažant, V., *Collection Czechoslav. Chem. Comm.*, **15**, 73–81 (1950) (in English).
257. Sosa, A., *Bull. soc. chim. biol.*, **29**, 833–836 (1947).
257a. ——, *ibid.*, **32**, 344–356 (1950).
257b. ——, *Compt. rend.*, **230**, 995–997 (1950).
258. Spielman, M. A., *J. Biol. Chem.*, **83**, 503–522 (1929).
258a. Stage, H., *Fette, u. Seifen*, **53**, 677–682 (1951).
259. Steger, A., and van Loon, J., *Rec. trav. chim.*, **54**, 149 (1935).
259a. Steinle, J. V., *Chemurgic Digest*, **11**, No. 6, 4, 1952.
260. Stenhagen, S., and Stenhagen, E., *J. Biol. Chem.*, **165**, 599–604 (1946).
261. Stock, E., *Farben Ztg.*, **19**, 1188–9 (1914).
262. Stodola, F. H., and Anderson, R. J., *J. Biol. Chem.*, **114**, 467–472 (1936).
263. ——, *et al.*, *J. Biol. Chem.*, **126**, 505–513 (1938).

264. Stossel, E., and Zerner, E. (to Mathieson Alkali Works, Inc.) U.S. Patent 2,431,842 (1947).
265. Straman, F. J. S., *Pharm. Weekblad*, **64**, 52–69 (1927).
265a. Stürcke, H., *Ann.*, **223**, 283 (1884).
266. Sundwik, E. E., *Z. physiol. Chem.*, **53**, 365 (1907).
267. Sweet, D. F., *Chem. Ind.*, **47**, 3 (1940).
268. Swenson, O. J., U.S. Patent 2,450,655 (1948).
269. Takeshita, Y., and Maruyama, S., *J. Nippon Oil Technol. Soc.*, **2**, No. 1, 27–29 (1949).
269a. Tamura, S., *Z. physiol. Chem.*, **87**, 85–114 (1913).
270. Tange, Ume, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **14**, 275–277 (1930).
271. Tassilly, M. E., *Bull. soc. chim.*, **9**, 608–615 (1911).
272. Teng-Han Tang, *et al.*, *J. Chem. Eng., China*, **6**, 19–22 (1939) (in German); [*Chem. Abstracts*, **35**, 7222 (1941)].
273. The Dispensatory of the United States of America, 24th Ed., by Osol, A., Farrar, G. E., *et al.*, Philadelphia, J. P. Lippincott Company.
274. Thorpe, Sir. E., "Dictionary of Applied Chemistry," Revised, London, Longmans, Green & Co., 1912.
274a. Tiedt, J., and Truter, E. V., *Chemistry & Industry*, **1952**, 403.
275. Tonn, W. H., Jr., and Schoch, E. P., *Ind. Eng. Chem.*, **38**, 413–415 (1946).
276. Toyama, Y., *Chem. Umschau Gebiete, Fette, Öle, Wachse, Harze*, **29**, 237–240, 245–247, (1922); **31**, 61–67, 153–154 (1924).
277. ——, *J. Soc. Chem. Ind., Japan*, **30**, 519–527 (1927).
278. Transcoso, A. de Medeiros (Inst. oleos, Rio de Janeiro, Brazil), *Bol. divulgacao inst. oleos*, No. 3, 13–20 (1945); *Rev. quim, ind.*, **17**, No. 192, 21–23 (1948).
278a. Tsuchihashi, R., and Tasaki, S., *J. Chem. Soc. Ind., Japan*, **21**, 117 (1918).
279. Tsuchiya, T., *J. Nippon Oil Technol. Soc.*, **1**, No. 2, 24–26 (1948); **1**, No. 3, 24–29 (1948); **1**, No. 4, 4–6 (1948).
279a. ——, *ibid.*, **1**, No. 2, 10–18 (1948).
279b. ——, *ibid.*, **1**, 1–6 (1948).
280. Tsujimoto, M., *Chem. Umschau*, **30**, 33–36 (1923).
281. ——, *Bull. Chem. Soc. Japan*, **10**, 212–219 (1935).
282. ——, *ibid.*, **6**, 325 (1931); *J. Soc. Chem. Ind., Japan*, **42**, Suppl. binding, 396 (1939).
283. Tsutsumi, S., *J. Nippon Oil Technol. Soc.*, **1**, No. 3, 12–15 (1948).
284. Tutin, F., and Clewer, H. W. B., *J. Chem. Soc.*, **105**, 1845–1858; *Proc.*, **30**, 210–211 (1914).
285. Tuzimoto, M., *J. Soc. Chem. Ind., Japan*, **42**, Suppl. binding, 396 (1939).
286. Ueno, S., *et al.*, *J. Soc. Chem., Ind., Japan*, **44**, 689–691 (1941); [*Chem. Abstracts*, **42**, 2119 (1948).
286a. ——, and Tsuchikawa, H., *J. Soc. Chem. Ind., Japan*, **45**, 203–206 (1942).
287. ——, *et al.*, *J. Soc. Chem. Ind., Japan*, **47**, 604–607 (1944); *Chem. Abstracts*, **42**, 6555 (1949).
288. Ullman, F., "Enzyklopadie der technischen Chemie," Berlin, Urban and Scwarzenberg, 1914.
288a. ——, *ibid.*, Revised, 1922.
289. Ultée, A. J., *Pharm. Weekblad*, **52**, 1097–1101 (1915).
290. ——, *ibid.*, **61**, 1118–1120 (1924).
291. ——, *Bull. Jard. bot. Buitenzorg* (iii) **5**, 105–106 (1922).

292. ——, *ibid.*, 241–243; *Chem. Centr.*, **1923**, I, 1191.
293. "United States Dispensatory," 19th Ed., Revised by Wood, H. C., Remington, J. P., and Sadtler, S. P., Philadelphia, J. P. Lippincott Co., 1910.
294. "United States Pharmacopoeia, XI," Printed by Mack Printing Co., Easton, Pa., Agent, 1936.
295. ——, *ibid.*, XIV Edition, 1950.
296. Utz, F., *Rev. Fett-Harz. Ind.*, **13**, 249–250, 275–277 (1906).
297. Valenta, E., *Z. f. anal. Chem.*, **23**, 257 (1884).
297a. Vallernaud, J. P. A., U.S. Patent 2,350,000 (1944).
298. Van Beckum, W. G., Weyerhauser Timber Co., Longview, Washington, correspondence.
299. Vansell, G. H., and Bisson, C. S., U. S. Dept. Agr. Bur. Entomol. Plant Quarantine, E-495, Feb., 1940.
300. Velick, S. F., *J. Biol. Chem.*, **154**, 497–502 (1944).
300a. ——, and English, Jr., J., *J. Biol. Chem.*, **160**, 473–480 (1945).
301. Velluz, L., and Lederer, E., *Bull. soc. chim. biol.*, **27**, 211–218 (1945).
302. Venton, C. B., *Intern. Sugar J.*, **51**, 55–58 (1949).
303. Verkade, P. E., and Cooper, J., *Rec. trav. chim.*, **46**, 528 (1927).
304. Vesterberg, K. A., and Vesterberg, R., *Arkiv. Kemo. Mineral Geol.*, **9**, No. 27, 17 pp. (1926); [*Chem. Abstracts*, **20**, 1994 (1926)].
305. Viard, M. J., *Parfumerie de France*, No. 36, 33–37 (1926).
306. Wagner, H., *Z. Intersuch. Lebenam.*, **76**, 1–20, 449–475 (1938); **77**, 225–247 (1939).
306a. Waller, C. W., and Gisvold, O., *J. Am. Pharm. Assoc.*, **34**, 78–81 (1945).
307. Walmesley, W. N., *Bull. Pan. American Union*, **73**, 31–42 (1939).
308. Walsh, C. L., *et al.*, British Patent 576,900 (1946).
309. Warming, E. (Univ. Copenhagen), "Oecology of Plants," Translated by Percy Groon (London), Oxford, Clarendon Press, 1909.
310. Warth, A. H., "The Chemistry and Technology of Waxes," 1st Ed., p. 105, New York, Reinhold Publishing Corporation, 1947.
311. ——, *ibid.*, p. 133.
311a. ——, *ibid.*, p. 136.
312. Warth, A. H., Jr., unpublished analytical determinations.
313. Weber, E., *Ber. schweiz. botan. Ges.*, **52**, 111–174 (1942).
314. Weinhagen, A. B., *Z. physiol. Chem.*, **100**, 159–166 (1917).
315. Weitkamp, A. W., *J. Am. Chem. Soc.*, **67**, 447–454 (1945).
316. Weitkamp, A. W., and Brunstrum, L. C., *Oil & Soap*, **18**, 47 (1941).
317. ——, and Oblad, A. G. (to Standard Oil of Indiana), U.S. Patent 2,325,818 (1943).
318. Wells, F. B., U.S. Patent 2,450,403 (1948).
319. Whitby, G. S., *J. Chem. Soc.*, **1926**, 1458–1465.
320. Whyte, D. E., and Hengeveld, *B.*, *J. Am. Oil Chemists' Soc.*, **27**, 57–60 (1950).
321. Wieghard, W., and Anderson, R. J., *J. Biol. Chem.*, **126**, 515-526 (1938).
322. Wilder, E. A., U.S. Patent 2,456,661 (1948).
322a. Wilder, E. A., U.S. Patent 2,471,805 (1949).
322b. Winterstein, A., and Hämmerlee, W., *Z. physiol. Chem.*, **199**, 25–37 (1931).
323. Woodward, E. R., and Malstrom, I., U.S. Patent 2,481,463 (1949).
324. Wynberg, A. French Patent 397,843 (1909).
325. Yamamoto, R., and Ninomiya, M., *J. Agr. Chem. Soc., Japan*, **12**, 26–28 (1936).
326. Yamazaki, R., and Matumoto, I., *Kwagaku to Kogyo* (*Science and Ind.*) **16**, 427–429 (1941).

327. ——, and Ogawa, G., *Kwagaku to Kogyo* (*Science and Ind.*), 417–419, 440 (1941); *J. Soc. Chem. Ind. Japan*, **44**, Suppl. binding, 241 (1941) (in English).
328. Yasunaga, S., *J. Pharm. Soc. Japan*, **72**, 869–871 (1952).
329. Zellner, J., *Monatsh*, **46**, 309–331, 611–630 (1926); **47**, 151–178, 659–679 (1926); **48**, 470–490 (1927).
330. Zetsche, F., and Lüscher, E., *J. prakt. Chem.*, **150**, 68–80 (1927).
331. ——, and Sonderegger, G., *Helv. Chim. Acta.*, **14**, 632–641 (1931).
332. Zöllner, W., *Farben, Lacke, Anstrichstoffe*, **3**, 385–390 (1949).

4. Fossil Waxes, Earth Waxes, Peat Waxes, Montana Waxes, and Lignite Paraffines.

Fossil waxes are waxes associated with fossil remains which have not been bituminized, that is, converted to hydrocarbons by geological change. *Bitumen* is the name applied by the Romans to the various types of natural hydrocarbons; in the modern use of the word it is in a sense restricted to the solid or semisolid hydrocarbons. *Montana wax*, a fossil wax, is often erroneously classed as a bitumen.

A fossil wax, chemically speaking, is composed largely of saponifiables, such as esters of fatty or wax acids. Fossil waxes, of nearly pure ester composition, are occasionally found in fragments of prehistoric plant life, still in a state of preservation as to the original wax constituents. Such pure ester waxes are only obtainable in minute quantities but are of great interest to the paleontologist, since they constitute the link between the living plant cell and the fossil remains which have undergone material change through the agency of heat and pressure in geological epochs of time.

Not far removed from fossil wax of the above described prehistoric plant life is montana wax which is an ester wax partially bituminized. Montana wax is commercially extracted from the nonasphaltic insoluble pyrobitumen with which it is associated, by means of an organic solvent. *Bitumens* as a class include native mineral waxes such as ozocerite, native asphalts, and asphaltites. They are fusible and soluble in carbon bisulfide, in contrast to the *pyrobitumens* which are fusible but insoluble in this solvent. The pyrobitumens are either asphaltic like elaterite and oil shale, or nonasphaltic such as those in peat, lignite, bituminous coal, and lignite shale.

Earth waxes is a generic term given to native mineral waxes or wax bitumens associated with earth deposits of a sedimentary nature belonging to the Tertiary period. They are almost completely composed of hydrocarbons sapropelic in origin. *Ozocerite* is a wax typical of this character.

Lignite paraffin waxes, or lignite paraffines, are waxes produced as a by-product in the recovery of fuel and lubricating oils from the dry distillation of lignitic coal, or brown coal. The native wax of these coals is largely composed of esters with bitumen as a minor constituent. In the Saxon and Thüringia district in continental Europe the bituminous mineral, or lignite,

referred to as pyropissite, was at one time the source of a great paraffin industry. Molinari[21] remarks that the valuable source of the native wax (ester wax) had been squandered by distillation when it might have been extracted in much higher yield by direct use of a suitable solvent, and the mass purified by treatment with fuming sulfuric. Provincially the native wax is known as *bergwachs*, which translated is "mountain wax." *Lignite waxes* are, however, refined on an extensive scale from the brown coal deposits in Upper Silesia, a less favorable source for montana wax (*bergwachs*).

FOSSIL WAXES

Waxes from Low Forms of Marine Life

Generally speaking, the waxes obtainable from the low forms of marine life are lipid waxes, and contain fatty acids, sterols, phosphatides, and hydrocarbons. Lovern[15] reported the relative proportions of fatty acids in the so-called fat of a marine alga, as follows: saturated acids—C_{12}, 0.3; C_{14}, 0.2; C_{16}, 7.3; C_{18}, 1.9 per cent; unsaturated acids—C_{14}, 0 5; C_{16}, 5.0; C_{18}, 62.5; C_{20}, 13.5 per cent. As in the fresh-water zoöplankton, the percentage of unsaturated acids is high for the marine types of algae. Hilditch[12] states that seaweed wax is obtained from deposits of algae which have been converted into material analogous to peat or lignite, and that the wax contains esters of the higher saturated alcohols and fatty acids of the C_{20}, C_{22}, and C_{24} series; that is, *eicosanoic*, *docosanoic*, and *tetracosanoic acids*. These acids are also commonly called *arachidic*, *behenic*, and *lignoceric* acids.

Let us consider for a moment the waxy constituents of living algal plants. Algae such as zoöplankton and phytoplankton contain 17.3 and 15.5 per cent respectively of saturated acids of high molecular weight, and 53.2 and 2.1 per cent respectively of highly unsaturated acids. The chlorophyceae contain C_{14} to C_{18} saturated acids, and C_{14} to C_{22} unsaturated acids. These living micro-plant organisms fossilize eventually so that the unsaturated acids disappear, and wax esters form along with the hydrocarbons.

Of the constituents common to algal plants, Heilbron and associates[10] have isolated both sterols and hydrocarbons. Algal plants contain a sterol, either *sitosterol* or *fucosterol*, or both. Much of the sterol is combined with a fatty acid. They also contain *hentriacontane* (m. 67°C), and terpenes. Sirahama[37] reported on a sterol he named *pelvesterol*, several hydrocarbons ($C_{18}H_{30}$, $C_{21}H_{38}$, $C_{20}H_{34}$), and hydrocarbons of the terpene group, which he found as constituents of the unsaponifiable matter obtained from marine algae. He also reports that pelvesterol is obtainable from various species of seaweed. In its crude form the sterol consists of yellowish red silk-fiber-shaped crystals which yield colorless needle-shaped crystals on purification. Sources of pelvesterol-bearing low orders of marine life are as follows:

Species	Physical Constants
Pelvetia wrightii	M.P. 122°C, $[\alpha]_D$ −39.0°
Fucus evanescens	M.P. 122°C, $[\alpha]_D$ −39.8°
Laminaria ochotensis	M.P. 122°C,
Hijikia fusiforma	M.P. 122°C, $[\alpha]_D$ −39.5°
Alaria crassifolia	M.P. 124°C, $[\alpha]_D$ −41.6°
Cystophyllium hakodatense	M.P. 124°C, $[\alpha]_D$ −41.5°

Pelvesterol appears to be identical to fucosterol, $C_{29}H_{47}OH$ [$b_{0.2}$ 220–230°C, m. 124°C, $[\alpha]_D$ −38.2°], isolated by Heilbron *et al.*[9] from the bladderwrack rockweed, *Fucus vesiculosis*. These investigators obtained 0.2 per cent of fucosterol from the dry seaweed by extracting with alcohol, and saponifying the extract partitioned off by petrolic ether. Sirahama proposed the name "phycophosphatides" for the phosphatides of seaweeds and "phycophane" for the brown pigments contained in them.

Kramer and Pontonié in 1906–1907 hypothesized that the primary material of petroleum was the algae which were abundantly laid down in all epochs and which today are accumulating in marshy places. These algae, during thousands of centuries under the action of pressure and heat, could undergo transformations of chemical change, leaving a so-called algae wax which is converted into petroleum. In this manner, petroleum would be formed through the years, and is perhaps being formed now. The conversion of the wax to petroleum appears to take place in the cold under high pressure, rather than in the hot by distillation.

Bituminization of Water Organisms

With animal matter and genuine water organisms, for instance oil-bearing algae and plankton, bituminization takes place in which liquid petroleum is formed, and subsequent metamorphic changes lead to the formation of native solid bitumens, i.e., native mineral waxes. Materials furnishing the bitumens are preferably deposited in stagnating water, and there yield slime (sapropel) in which components are often remarkably preserved after thousands of years. It is the sapropels which are the source of petroleum. Drainless basins like the Caspian Sea afford favorable conditions for the production of sapropel as well as salt deposits. Among the sapropelites, one from the Tertiary period (glacial epoch of the Cenozoic era) resembles a dried and jelly-like sapropel (saprokohl), and contains about 50–57 per cent carbon, 6–7 per cent hydrogen, 4.5–6.5 per cent nitrogen, and a residue rich in oxygen.

Liquid hydrocarbons have been discovered in Recent sediments taken below the floor of the Gulf of Mexico. Age determinations carried out at the Lamont Geological Observatory at Columbia University indicate an age of 11,800 to 14,600 years for the hydrocarbons extracted from several

sections of the Grand Isle, Louisiana, core of Recent sediments. The quantity of free hydrocarbons in dried sediments is less than 190 parts per million, but nevertheless significant. The paraffin-naphthene content of the organic matter in Recent sediments increases with depth below the marine floor. It is worthy of note that paraffins and naphthenes have been found in extracts from laboratory cultures of marine bacteria.

Lignite Fossil Waxes

The liptobioliths, source of peat and montana waxes, originate in the Tertiary period. In 1929 Legg and Wheeler[14] in their study of fossil plant cuticles, particularly the liptobiolith known as Russian *papierkohle*, made comparison with the modern plant cuticle, such as sisal agave, *Agave sisalana*, which latter could be resolved into water-soluble 10, wax 20, cellulose 15, and cutin 55 per cent. The wax from the cuticle consists chiefly of *montanyl* and *melissyl alcohols*. The cutin upon destructive distillation gave about 20 per cent of hydrocarbon, *pentatriacontane* (m. 75°C).

An examination of cuticle from Russian papierkohle, in the form of crude material, was resolved into a composition of ulmins, soluble in ammonium hydroxide 35 per cent, insoluble in ammonium hydroxide 45 per cent, and fossil cuticles 20 per cent. No cellulose or water-soluble material was present but wax was found in quantities up to 4 per cent. The wax consisted chiefly of oleic and saturated hydroxy aliphatic acids. Dry distillation of the cuticle yielded saturated and unsaturated hydrocarbons, phenols, and oxygenated compounds.

Ciusa and his co-workers[5], University of Bologna, have studied the composition of the white incrustation observed by Simonelli in the transversal fracture of the trunks composing the xyloid deposit of Fogano, near Montepulciano. The component, $C_{15}H_{20}$, is readily soluble in organic solvents, melts at 61–62°C, boils at 314–316°C (b_{23} 208–210°C), and was shown to be a new species of mineral, which they named *simonellite*. Samples of lignite from Terni showed a hydrocarbon incrustation which melted at 71–72°C, or 74–75°C after purification; had the composition $C_{20}H_{34}$; and was not unlike *bombicite*. From another source they recognized a lignite hydrocarbon with a C_{24} composition.

The fossil wax from Monte Falo near Savigno, which had been previously studied by Bombicci, was reported by Ciusa and associates[5] as crystallizing in white, yellowish, or gray scales which melted at 47–49°C, or 50–52°C after crystallization from ethanol. The wax when fractionated *in vacuo* yielded the hydrocarbons, $C_{23}H_{48}$ (m. 47–47.5°C); $C_{24}H_{50}$ (m. 50.7–51.3°C); and $C_{26}H_{54}$ (m. 56–57°C). These investigators concluded that the fossil wax is paraffin and Bombicci's hypothesis that it is formed by the evaporation of petroleum is justified.

Combustible Organogenic Rock Formations

The combustible organogenic rock formations were divided by Stremme[41] into (1) *sapropelites*, derived mainly from true water organisms and their excreta; (2) *humus formations*, derived from land plants (bog vegetation); and (d) *liptobioliths*, derived from resiniferous and wax-resiniferous land plants and humus deposits.

The sapropelic rocks (saprolites) originating in the Paleozoic era are highly carbonized; they are less so in the Mesozoic era, and bituminized in the Tertiary and the Quaternary periods of the Cenozoic era, which covers the past million years. Humus formations originating in the Paleozoic era are still more carbonized (80–95 %C). Test borings at the bottom of deep peat deposits in the United States reveal a fine-grained layer formed from the decomposition of the algae. This material is known as *algae peat* or *dropperite*, and is not unlike the sapropel previously referred to.

The liptobioliths, source of *peat* and *montana waxes*, originated in the Tertiary period. Resin and wax-secreting vegetation was lacking in the Carboniferous period and only appeared later. *Pyropissite* is to be regarded as the residual resin and wax-resin of plants, which under the conditions of peat formation and subsequent alteration in the latter part (Permian period) of the Paleozoic era, have afforded brown coals, between which and pyropissite all gradations exist.

The atomic ratios for various basic materials of coal are considered to be C_2H_3O for lignin, $C_{16}H_{16}O$ for resins, $C_{18}H_{18}O$ for fatty acids, and $C_{35}H_{59}O$ for waxes. During the formation of coal a slow action of oxygen results in an exothermic oxidizing of hydrogen, leading to enrichment of the carbon content; this carbonizing process is referred to as "Inkolung."

EARTH WAXES

Natural Occurrence of the Earth Waxes

Typical of the earth waxes is the *ozocerite* of Galicia. The Galician beds have been worked at great depths, 1000 feet or more, and the deeper the mining the softer and more paraffin-like the ozocerite. There lumps of it are found in irregular lodes and clefts or in pockets formed in the salt clay. The largest mines, and these are deep underground, are those of the northern foothills of the Carpathians, particularly in Boryslaw near Drohobycz. Abundant deposits are also found in the Wallachian side of the range, and in smaller deposits along the Caspian under the name of "neftgil."

The mining of ozocerite in Galicia is comparatively simple. Formerly merely well shafts were sunk, but today it is mined in the manner of coal, by deep underground operations. The mined ozocerite is dark in color, the lumps intermingled with earthy impurities; it is cleaned by hand, or by melting. In Galicia sources of commercial supply are at Boryslaw, Dwein-

iacz, and Starunia. It is said that at one time as much as 20,000 tons per annum was mined in Galicia, but the production is far less than that amount at the present time.

Where ozocerite is located the shale is soft and it is believed that the shale in geological ages acted as a molecular filter and condensator. According to one hypothesis, small hydrocarbon molecules were converted into large ones by a sort of polymerization process leaving a residue of wax, which occasionally is accompanied by small amounts of oil. The colloidal earth which accompanies ozocerite is salty, which indicates the existence in an early geological period, probably Carboniferous, of a water hydrostatic pressure. The greater the pressure to which ozocerite has been exposed, the lighter its color and greater its hardness. We would expect and do find the hardest wax (marble wax) to be pressed up against the overlying rock.

The earth waxes after being fully refined are in many respects similar to microcrystalline waxes of a similar melting point obtained as raffinates in the distillation of certain petroleums, and which appear on the market as petroleum *ozokerites*. The earth waxes consist of an aliphatic series of straight-chain and branched-chain hydrocarbons, with some oxygenated resinous bodies when not fully refined. What is known commercially as *ozocerite* is the particular earth wax that is mined in eastern Europe. The earth waxes found elsewhere, as for example in the United States, are of a somewhat different hydrocarbon composition from ozocerite, and exhibit differences in physical behavior.

The origin of earth waxes is believed to be closely linked to that of petroleum, which is derived from the carbonization and concomitant distillation of animal or vegetable remains, under the heat and great pressure deep under the earth's surface, during one of the middle periods in geological history. One theory is that petroleum in many regions was forced by hydrostatic pressure upward through porous sandstone capped by impervious shale.

Specimens of earth waxes have been obtained from Scotland, Northumberland, and Wales, as well as from Russia (the Kaukasus, Tscheleks, Turkestan), and from Iran (Fergona). The largest workable deposits are those of ozocerite in the Carpathian Mountains. In the United States a considerable tonnage of earth wax has been mined at Soldiers Summit, Utah. There are also deposits of earth waxes in South America.

Hardness of Earth Waxes

The hardness of the earth waxes varies a great deal according to the source and whether they are crude or refined, the latter being softer. An approximation of the hardness may be determined with the aid of a Shore durometer (scale 0–100)[47].

Ebony Utahwax has a durometer hardness at 25°C of 95, whereas the

refined yellow Utahwax has a hardness of 70. Pure white Galician ozocerite has a hardness of 53. The addition of paraffin wax of 128/130°F melting point to ozocerite increases its hardness and toughness. An artificial ceresin made with ⅓ ozocerite and ⅔ paraffin wax (128/130°F m. pt.) has a hardness of 60. White microcrystalline wax of 160°F m. pt. has a hardness of 50, and bleached beeswax of 60.

The waxes compounded from paraffin wax and ozocerite when properly proportioned have a dense microcrystalline structure much desired for many purposes. For most purposes paraffin wax of 128–130°F melting point is also greatly improved in its physical characteristics by the addition of 5 to 15 per cent ozocerite.

Ozocerite of Commerce—Galician

Ozocerite is a name apparently derived from the Greek words *ozo* "to emit odor" and *kerite* which is "wax." About the middle of the last century, it is said, came news from Galicia of the existence of a natural earth wax, which had some of the characteristics of beeswax. At or near its source it had been used for many years for the making of axle grease, leather dressing, and as a fuel for heating.

The mined ozocerite upon melting is freed from earthy impurities and cast into forms resembling truncated cones that weigh about 40 kilograms. The qualities produced at the mine are the "hardgreen," "hardbrown," and "softblack," which are graded by the following congealing points: "hardgreen," 74–76°, 70–72°, and 66–68°C; "hardbrown," 70–72° and 66–68°C; "softblack," 55°C. The melting points are 4° above the congealing points. The cleaned ozocerite has an amorphoid or microcrystalline structure, and a density (d^{15}) of 0.900 to 0.907. Ozocerite when bleached has a similar physical structure but is of a little higher density, namely 0.910 to 0.920 at 15°C.

Refining of Ozocerite. In 1870 Pilt and Ujhelyi found that a simple treatment of mined ozocerite with concentrated sulfuric acid, followed by decolorization with animal charcoal, yielded a product of great value in the arts and industries. Molinari[21] has described the refining process as follows: "The refining is carried out in large iron boilers holding up to 3000 kilos of the crude wax, which has been melted free from earthy and stony matter at the mines, half a meter being left free to take the scum which forms. The fused mass is kept at 115–120°C for 4 to 5 hours and is stirred to liberate all the water. The required amount, 15–25 per cent of fuming sulfuric (78 per cent SO_3), is then added in a thin stream to the mass, which is thoroughly stirred meanwhile; the temperature slowly rises to 165°, then to 175°C, the oxidizable impurities separating as a black asphaltic mass, and the excess of sulfuric acid evaporating. The vessel is covered and provided with a draught-pipe to carry off the acid vapors. The mass is allowed

to cool slowly, being neutralized with residues from the manufacture of ferrocyanide, decolorized with animal black and sent to the filter presses. The mass obtained is still slightly yellow and is whitened by further treatment with sulfuric acid. When beeswax is to be imitated, quinoline yellow or other suitable coal-tar dye is added."

Acid-treated ozocerite which has received no additional decolorizing treatment is referred to as *yellow refined ozocerite*, or *once bleached ozocerite*. The fully refined wax is known as *double bleached*, or *white refined ozocerite*.

No bleaching of ozocerite is conducted at Boryslaw, Poland. The black wax reaches the port of Trieste, or Fiume, and from there is exported elsewhere. The wax bleached in Italy became known as "ceresin," but it was very often blended with white refined paraffins before being exported to other countries.

Ozocerite crude on distillation in a current of superheated steam yields a candle-making material resembling paraffin wax obtained from petroleum and shale oil, but of higher melting point (64–65°C) than ordinary paraffin, and therefore of greater value if the candles made from it are to be used in hot climates. There are also obtained in the same distillation light oils and a product resembling "Vaseline." The residue left in the stills consists of a hard black waxy substance, which when incorporated with india rubber is employed under the name of *okonite* as an electrical insulator. From the residue a form of material known as *heel-ball*, used to impart a polished surface to the heels and soles of boots, is also manufactured.

There is probably no wax which is subjected to adulteration as much as ozocerite. Therefore, methods of detecting such adulteration are worthy of consideration when this wax is purchased from any other than a very reliable source. The melting point, the specific weight, and the structure, i.e., the feel, of an ozocerite, are determinants. The addition of small amounts of paraffin wax, 5–10 per cent, to ozocerite almost defies detection, since ozocerite itself differs slightly in its physical constants depending upon its origin.

Physical Properties of Ozocerite. The pure ozocerite has a melting point of 74.4–75°C (166–167°F). If only 5 per cent of plain paraffin wax has been added to ozocerite to assist in its bleaching, it is difficult to detect it, since the ozocerite will melt at 166°F.

Per Cent Paraffine 132/134°F (AMP)	Melting Point (°F)
5	166
10	164.5
15	163
20	161.5
25	160
40	155
60	147.5
100	133

A sample of crude from Boryslaw, Poland melted at 172–174°F. It was of a very dark brown color. A sample of cream color snowflakes from Boryslaw melted at 168–170°F. Another, but more yellow, sample, melted at 170–172°F.

Pure white ozocerite when compounded with crystalline paraffin of 128–130°F melting point in the proportion of 1 to 3 produces a wax melting at 158°F. The latter mixture has many of the same properties as ozocerite except for the somewhat lowered melting point, and is much less expensive. There is unfortunately a great temptation to adulterate ozocerite with a proportion of paraffin wax and to undersell jobbers marketing the 100 per cent pure ozocerite.

Pawleski[24] studied the behavior of ozocerite with solvents. The wax tested was one that had been distilled in a current of superheated steam from crude ozocerite. It had a specific gravity (d^{20}) of 0.9170, melted at 64–65°C, and solidified at 61–63°C. One hundred ml of solvent dissolved the following amounts of ozocerite wax expressed in grams: petroleum ether 8.48, turpentine 5.21, cumene, 3.72, xylene 3.43, toluene 3.34, chloroform 3.61, benzene 1.75, isobutyl alcohol 0.228, acetone 0.209, amyl alcohol 0.164, methanol 0.056, glacial acetic acid 0.063, formic acid 0.015. The following weights of solvent were required to dissolve completely 1 part of ozocerite wax: Carbon disulfide 7.6, petroleum ether (b.p. up to 75°C) 8.5, turpentine 16.1, xylene (b.p. 135–143°C) 25.1, toluene (b.p. 108–110°C) 26.1, chloroform 41.3, benzene 50.3, ethyl ether 50.8, isobutyl alcohol 352.9, acetone 378.7, ethyl acetate 419.0, ethanol 453.6, methanol 1447.5, methyl formate 1648.7.

On the whole ozocerite is much less soluble in various solvents than paraffin wax. Carbon tetrachloride (100 ml) dissolves 11.78 grams of paraffin (130°F m.p.), but only 1.95 grams of ozocerite. Chloroform, amyl alcohol, benzene, acetone, and ether all dissolve nearly five times as much paraffin as ozocerite.

Ozocerite has an excellent moisture resistance, a low index of refraction, and a very low conductance for heat. Its coefficient of expansion is 0.001 per 1°, between 1° and 50°C. The solidification point of pure Galician ozocerite is 73°C (163°F), cloud point 76° (169°F), boiling point above 300°C (572°F). The dielectric strength is in excess of 30,000 volts across a $\frac{1}{10}$-inch G. E. Standard gap. Its dielectric constant (permativity) is 2.03, its power factor 0.03, and its resistivity 36×10^6 megohms across a 1-cm cube.

A pure white refined form of Galician ozocerite that has appeared on the market is known under the trade name of "*JAA Wax*," the initials being impressed on each slab so as not to mistake its identity. "JAA Wax" has a melting point of 75°C (167°F). Pure white ozocerite in the melted form has

a much lower specific gravity (d^{98}), namely 0.753–0.796, than beeswax (0.822), and contains no saponifiable matter.

Chemical Composition of Ozocerite. Ozocerite consists of straight-chain, branched-chain, and closed-chain hydrocarbons. It is thought that it has large polymethylene rings which might be considered as double chains. Ceresins, of which Boryslaw ozocerite is a type, retain their oil very tenaciously and cannot be separated therefrom by the usual process of filtering and pressing. At similar melting points, the ceresins have a much higher molecular weight, specific gravity, viscosity, boiling point, and nitrobenzene point than the paraffins, which consist chiefly of normal straight-chain hydrocarbons. Before refining, ozocerite contains an appreciable amount of oxygenated resinous bodies.

Ozocerite has a delicate crystalline structure, the crystals being of needle or short plate shape, microcrystalline. Chemically the ceresins are much less stable than solid paraffins and react readily with fuming sulfuric acid or with chlorosulfuric acid, a fact which has been interpreted to indicate an *isoparaffinic* structure. On account of their high boiling points they can be partially separated from paraffin wax. Molecular weights corresponding to the formulas $C_{37}H_{76}$ to $C_{53}H_{108}$ are found for these branched-chain hydrocarbons. The monoclinic needle-like variety of crystals are believed to consist of open-chain paraffins with short branches. and the triclinic plates of saturated cyclic hydrocarbons with long chains.

Use of Ozocerite in Industry. Ozocerite as well as the American ozokerite, the latter of petroleum origin and refining, easily mixes on melting with oils and fats of most any description, and with waxes such as paraffin, carnauba, japan, bees, montan, etc. It mixes with stearine, asphaltum, and rosin. It readily dissolves in distillates from coal or petroleum, producing on cooling a product of salve-like consistency. Of all the waxes ozocerite has the greatest affinity for oil, or absorbs it the best. Because of its valuable properties, ozocerite has been extensively used in many industries.

Nitsche[22] has discussed the valuable homogenizing properties of ozocerite in restraining visible crystallization at the surface of paraffin wax pastes in which the ozocerite has been incorporated, although he also notes that certain artificial ozokerites recovered from the products of the Fischer-Tropsch benzin synthesis behaved similarly in restraining crystallization and evaporation of solvent. He also pointed out the injurious effect of acid refinining on the homogenizing properties of ozocerite; and less harmful bleaching by adsorbent agents is advocated where possible.

A good shoe polish or cream should be of a salve-like consistency, should not exude oil, and should produce a brilliant gloss. The luster of such a paste polish is furnished by hard waxes like carnauba but the salve-like

consistency and oil-retaining quality are best obtained from ozocerite. *Paraffin wax*, unless used as a minor component of paste polish, may cause cracking around the edges of the box, after the paste dries through exudation of the oil. This is also true of paraffin wax in floor polishes and leather dressings.

In the manufacture of pharmaceutical and cosmetic preparations it is highly desirable to use a neutral, white, odorless, tasteless, amorphous wax. Ozocerite is of great value in these preparations. The electrical industry has always been a large consumer of ozocerite, crude or refined, as it is an excellent insulator. The surface resistance is said to be three to seven times that of ordinary paraffin wax and the transient resistance 220 to 1700 times greater. The crude or refined wax is used in accumulators, dry batteries, cable boxes, and dynamo armatures. Certain hard rubber compounds for electrical purposes contain 2–5 per cent ozocerite. Ozocerite makes an excellent cable wax because of its durability, elasticity, resistance to marked changes in temperature, and its insulating properties. In cable coating the ozocerite is preheated for several hours at a high temperature before applying.

Fat compounds prepared from paraffine and tallow, or the like, are used in their melted state to impart to tanned leather a polish, color, moisture-proofness, elasticity, and toughness. By adding ozocerite to these compounds they can be greatly improved, resulting in a better quality of leather with increased weight. Ozocerite also prevents the paraffin wax and stearin from causing a bloom or spew after the leather has been drawn through the bath. It is advantageous to add as much as 25–30 per cent to the fat compounds.

In wax figure making ozocerite can be freely substituted for beeswax, and hence is of great value in that art. Its high melting point is advantageous. Hard paraffin waxes when used for this purpose prove unsatisfactory as they are dry and brittle and are apt to scale off. Ozocerite is also used in the making of tapers and candles.

Paper converters find ozocerite of value in the preparation of waxed glassines, waxed sulfite, laminated foil glassine, waxed oil paper, etc. It is of value in carbon paper manufacture because of its retention of oil in which the pigment or color is dissolved. Ozocerite is used in the manufacture of wax flowers and fruit, crayons, waxed matches, for impregnating corks and umbrella silk, and for steam packings. The "hard green" variety is used by electrotypers to secure sharp impressions, since this type of wax has a low coefficient of expansion and contraction.

Ozocerite is used in waterproofing cloth; the treatment forms one step in the finishing. The waterproofing solution may be formulated as follows: ozocerite 5, liquid petrolatum 5, and benzene 90 parts. After evaporation

of the benzene the waterproofing material contracts on the yarn, and leaves the pores of the cloth free and open, a desirable part of the finish. The waterproofing of pails, casks, and other vessels and utensils by ozocerite was patented as early as 1885 by Maxfield[19].

Polystyrene alkylated with a polymerized propylene can be mixed with ozocerite to produce a wax composition suitable for the impregnating and coating of fibrous products such as textiles, leather, wood, and papers for the purpose of improving the gloss, adhesiveness, hardness, tensile strength, and elongation characteristics (also see p. 518).

The unavailability of European ozocerite during and after World War II led largely to the substitution of American petroleum ozokerite for the earth wax (also see Artificial Ozocerites). The 1950 consumption of mineral waxes is estimated as 4,008,000 pounds. Of this amount 108,000 pounds is ozokerite. Imports of ozocerite, ceresin, and other mineral waxes (excluding montan) were over 800,000 pounds in 1939, with average price 18½ cents per pound.

Utah Ozocerite Wax

About fifteen hydrocarbon minerals occur in Utah, five of which are well known, namely, gilsonite, tabbyite, wutzellite, ozocerite, and rock asphalt. According to Bardwell *et al.*[1], gilsonite is limited to Uinta County, where it occurs as a filling in vertical fissures in the Green River calcareous shales of the Eocene epoch, and in limestones and sandstones. Tabbyite occurs in Tabby Canyon, Uinta County, in vertical fissures in Upper Tertiary sandstones and shales. Wutzellite, also known as elaterite or mineral rubber, occurs in an area between Indian Canyon and Sam's Canyon, north of Price, in vertical veins 1 to 22 inches wide. Utah ozocerite, also known as American mineral wax or more specifically *Utahwax*, occurs in an area west of Cotton, Utah County, in shales, shaly sandstones, and limestones, in the lower part of the Wasatch Teritary Formation, chiefly in fissures and spaces in zones of brecciation and jointing. Rock asphalt, or bituminous sandstone, occurs in large deposits in many localities. The various hydrocarbons are mentioned since there may be a generic relation among them[1].

A considerable amount of Utahwax, as the Utah ozocerite has been termed, is being mined by breaking it out of the seams with a pick, unlike the open mine method of winning ozocerite in Europe. In the deeper workings in the Utah mine the ore is brought to the surface and milled. It is then melted and refined later at the refinery to which the crude is shipped. The ore is of a black-brown color, and the first melts are black. The Ozokerite Mining Company of Grand Rapids, Michigan, works on a Utah mineral wax ore which melts at about 93°C (200°F). This is acid bleached to prepare uniform gradings for the market. The grades have included "Ebony

Utahwax;" "Still Run Utah No. 1," "No. 2," and "No. 3;" and a "Refined Yellow." The *Ebony Utahwax* is the hardest, and the "Refined Yellow" the softest of the gradings. The latter is sometimes referred to as "Double-Refined Plastic Utahwax," and it is rather orange-yellow in color. The structure of the waxes is microcrystalline but nearly amorphous.

Measurements of hardness of Utahwax by penetrometer with standard needle (110 g/15 sec/t°C) are given by the refiner as follows: 0.43 at 20°, 0.64 at 30°, 1.27 at 40°, 2.20 at 50°, and 3.80 at 60°C. To illustrate the toughness of the wax a 9-mm jacketed bullet fired with a velocity of 1400 feet per second at a 5-inch thick slab penetrated one inch and was shattered into fragments without cracking the slab.

With a Shore durometer the writer determined the hardness of the Ebony Utahwax as 95 to 73°F. The durometer hardness of Still Runs No. 1, No. 2, and No. 3 were 90, 85, and 80 respectively. The Refined Yellow was 70 in hardness. Utahwax has a density of 0.9414 at 6°, 0.9290 at 25°, and 0.8850 at 60°C.

Uses of Utahwax. Utahwax can be substituted to a great extent for the Galician ozocerite in many industries but not all. The Galician ozocerite has certain peculiar physical properties which are nonexistent in other waxes, as for example in wax blends where the ozocerite has a remarkable oil adsorption and decrystallizing effect and prevents softening of the other wax components at temperatures below the melting point.

Utahwax is less expensive than Galician ozocerite. It is used chiefly for electrical insulations; for waterproofing pails and other containers; for corks, steam packing, and gaskets; for impregnating fabrics; and for wax matches.

Ceresin

The word *ceresin* is derived from the Latin word, *cera*, meaning "wax" (beeswax), and *sine* meaning "without" or "free from." That is, ceresin is a material "free from wax" (beeswax). The Spanish words are *cera* and *sin* respectively, and have the identical meaning, hence the word *cerasin*. "Ceresine," spelled with a final "e," is a name sometimes applied to an imitation of the so-called genuine *ceresin*.

The term ceresin in a narrow sense of the word was applied to refined ozocerite. The broader use of the term as used by Ellis[8] to define ceresin by its composition rather than its source, means that ceresin may arise from wax bearing distillates of any kind, whether natural mineral (ozocerite), petroleum refining (*petroleum ceresin*), or lignite refining (cerasin).

The hydrocarbons of crude oil and of mineral waxes are largely *iso*paraffinic, namely straight chains with alkyl side-chain linkages. They are of higher molecular weight, greater hardness, higher specific gravity, and of a

more wax-like consistency than the hydrocarbons (pyroparaffin) distilled from the crude. The *iso*paraffins change to *normal* paraffins upon distillation (paraffin wax). By heating crude montan wax in the presence of a catalyzer (*kieselguhr*) and with avoidance of distillation, *iso*paraffins (protoparaffin) may be obtained. By prolonged heating the saponifiable matter almost disappears from the soft waxy product. The product has an iodine number of 24, acetyl value of 50, and after hydrogenation an acetyl value of 73. It contains saturated and unsaturated hydrocarbons, alcohols, and ketones, according to Marcusson[17]. By treating with concentrated sulfuric acid, mixing with fuller's earth, and extracting with benzene, a light yellow wax-like mass, identical in appearance with ceresin (m. 64–66°C, *n* 11.9), is obtained.

Ellis[3] states that at similar melting points, the ceresins have a much higher molecular weight, density, viscosity, boiling point, and nitrobenzene point than paraffin waxes. They have a very delicate crystalline structure, the crystals being of the fine needle or short plate type. Chemically the ceresins are much less stable than solid paraffins and react readily with fuming sulfuric or with chlorsulfonic acid, a fact which has been interpreted to indicate an *iso*paraffinic structure.

Although ceresin at one time was synomonous with ozocerite, it had to compete keenly with a similar isoparaffinic product (cerasin) produced by a low-temperature distillation process at Saxony and Thüringia, in which a wax recovered from detarred lignite was fused with semirefined ozocerite, and the whole bleached white. Factories in Meisel, near Darmstadt, and in Hamburg, are said to have produced various grades of *cerasin*, some of which contained bleached montan wax (ceresin) and 20 per cent or more of imported paraffine. The adulteration of ceresin with paraffine to the extent that a little carnauba wax had to be used to boost the melting point has led to the offering on the market of numerous grades of imitation ceresin waxes, some of which are even artificially colored (see Imitation Ceresin Waxes, p. 499).

Ceresin and petrolatum can be produced from ozocerite without the use of sulfuric acid as the purifying agent, namely by dissolving the melted *ozocerite crude* in gasoline or ligroin, heating the solution, and percolating it through activated clay. The percolate is then rectified; the tail fractions contain *petrolatum* and *white ceresin*, and the residue consists of *yellow ceresin*. The yield can be improved by extracting the ozocerite ore with gasoline or ligroin instead of boiling water.

Surakhansk Cerasin of Russia. Surakhansk cerasin when fully refined has a density (d_{20}^{99}) of 0.788; solidification point of 87.7°C (190°F), and a molecular weight of 625.5 calculated for $C_{45}H_{92}$, 632.6. It is a mixture of isoparaffins, consisting chiefly of $C_{45}H_{92}$ and some $C_{22}H_{46}$. It is to be noted

that Surakhansk cerasin is one of the highest melting point hydrocarbon waxes known.

PEAT AND MONTANA WAXES

Liptobiolithic waxes may be conveniently divided into two groups of which there are four subdivisions. Group (A) consists of *peat waxes*, and group (B) of *montana waxes*.

The wax obtained from peat, while primarily of a composition similar to that of the wax obtained from lignitic coal, or brown coal, has somewhat different physical characteristics. Peat wax of Eire is sometimes referred to as Irish montana wax, although the designation is not strictly correct. In its chemically treated or refined state it is customarily referred to as "montanin wax" or "mona wax." Generally speaking, the commercial designation "montan wax" for true montana wax refers specifically to the product "bergwachs" refined from lignite at the Riebeck Montan Works, Germany, or its equivalent. Other montana waxes carry a designation as to origin, such as "American montan (or montana) wax," "Devon montan (or montana) wax," or "Czeckosovakian montan wax," since these waxes are not identical to the Riebeck wax, the first "montan" wax to appear on the market.

Montana waxes in good yields are obtainable from certain lignitic coals that have a fixed carbon content of 21 to 23 per cent, and only small yields from subituminous coals, which are much higher in fixed carbon content, namely 36 to 45 per cent.

Peat Wax

One of the most valuable of all potential by-products of peat is a wax which has a relatively high melting point. Eirie's tremendous peat deposits, covering one-fifth of the land surface, represent an important natural resource aside from their value of fuel.

A crude peat wax fairly high in asphaltic constituents has been obtained from the peat of the Chatham Islands, New Zealand. The Chatam Island moorland covers 40,000 acres with an average thickness of 14 feet to the peat deposit. The peat will yield 9.4 per cent of a crude wax having a melting point of 73°C. The size of the peat deposit and its high wax yield may serve to illustrate the importance of a future peat wax industry.

Crude peat wax is the part of the bitumen left when the *crude resins* are separated from it. The solubility of *peat bitumen* in certain solvents decreases when the material is heated or stored for some time, since the crude resin in peat bitumen is easily polymerized. The part of the peat bitumen which is insoluble in petrolic ether is known as *asphalt*, or *polymer-bitumen*, and the product that is extracted directly from peat is termed *crude wax*.

Origin of Peat. The decay of algae and plankton organisms results in the formation of detritus which as the bed thickens, provides lower layers where oxygen is wholly lacking, a prime condition for a process that has been termed by Potonié[26] as "Fäulnis." Peat is the result of a stage in the conversion in which the metamorphic change of the detritus is incomplete but in which there is an enrichment of carbon. Hence the crude extract of peat contains not only wax, but a considerable amount of asphaltic like and resinous material as well. The liptoliths, source of peat wax, originate in the Tertiary period of the Cenozoic era.

According to Roquette[24], deposits of algal detritus (bog peat) in the Paraiba Valley, Brazil, contain considerable amounts of wax, which this investigator calls montana wax, and are recoverable by solvents. On dry distillation at 400–500°C the peat yields 30–40 per cent of hydrocarbons with a high content of paraffins.

Extraction of Peat Wax. In 1907 Zaloziecke and Hausman[48] reported that they had obtained a waxy substance by passing alcohol vapor through a tube filled with peat, and that when the alcoholic extract was permitted to cool, it deposited dark yellow flakes or powder with a melting point varying from 80 to 96°C.

In 1926 Reilly studied the thermal decomposition of Irish peat under reduced pressure. In the rapid distillation of dry peat in a vacuum, Reilly (and Pyne) obtained less gaseous products and more tar or paraffinic fraction than is the case in the distillation at the ordinary pressure. In 1930 Reilly[29] (and Donnely) reported that the low-temperature distillation of peat comparable with that of various types of coal yielded: tar 16.6 per cent, phenols 5.4 per cent, acetic acid 22.6 pounds, ammonium sulfate 17.4 pounds, and 8.6 per cent gas. Later Reilly (and O'Sullivan) mixed pulverized peat with one ninth its weight of chalk, and distilled the mixture at 550°C in an electrically heated retort. The chalk did not change the yield of tar nor its character. They were able to show through a careful study that the tar product is a function of the wax content of the peat. By extracting the wax portion from the peat and subjecting it to distillation the products obtained, that is, extractives with selective solvents (ether, alcohol, and acetone in this order), are not particularly different from those of wax-free peat. They concluded that over 40 per cent of the tar produced is derived from 10 per cent of wax in the powdered black peat.

In 1937–1939 Reilly and his co-workers[30, 31] reported that successful results could be obtained in the extraction of wax from Irish Highland peat by using azeotrope-like mixtures of solvents such as petroleum spirits with alcohols (methyl, ethyl, isopropyl, or propyl), which solvents may be recovered without interference from the wax or water in the solvent mixtures.

In 1940 Reilly and Emlyn[32] reported that a sample of peat which gave 8.4 per cent of crude wax with petroleum spirit, on extraction with a mixture of the same petroleum spirit mixed with isopropyl alcohol (70:30), yielded 10.6 per cent of extract. Of this 10.6, 2.0 per cent was readily ex-

tracted by cold alcohol, yielding mainly resinous matter; the remaining 8.6 per cent was similar to the crude wax obtained by petroleum spirit alone. The presence of moisture does not hinder the removal of the wax by petroleum hydrocarbons. Crude from peat, which may contain bituminous matter in considerable amount as well as nonpolar resins, has been given the name *mona wax*.

Crude peat wax recently obtained by benzene extraction of a Northumberland peat has been recovered in 12 per cent yield based on dry peat. According to the method of examination at the Fuel Research Station, it contains 30 per cent resin (methanol soluble), 35 per cent true wax (40–60°C light petroleum soluble), and 35 per cent asphalt (material insoluble in light petroleum). An oxidized peat wax is obtainable in 80 per cent yield from the true wax fraction by treatment with chromic acid. This refined wax is pale greenish yellow in color, quite hard and glossy, and of high melting point. The crude wax is brownish black in color like the early samples prepared by Professor McGrath, of the University of Cork.

According to Sundgrén and Rauhala[42] (Helsinki, Finland), bitumen has been extracted from Aitoneva machine-peat by a mixed solvent, benzene-ethanol (1:9). The bitumen was divided into *crude wax* and *crude resin* fractions by dissolving it in boiling hot ethanol (94.5%) and precipitating the crude waxes from the solution at −7°C while the crude resins remain in solution. For certain experiments the crude wax was recrystallized from ethanol at 20°C and the product thus obtained was called "purified wax."

Peats derived from cottongrass, *Eriophorum vaginatum* L.; Scotch heather, *Calluna vulgaris* L.; and bulrush, *Scirpus* spp. gave wax yields of 7 to 12 per cent, while sphagnum, *Sphagnum* spp., and reed, *Phragmites* spp. gave only 3 to 5 per cent, on benzene extraction as determined by Cawley and King[4].

A recent British patent [647,693 (1951)] granted to the Minister of Supply describes a process of converting air-dried peat to oxalic acid with the peat wax as an important by-product. Air-dried peat is added while stirring to 4 parts of 85 per cent nitric acid, and after standing the resulting sludge containing *peat wax* is separated, washed with water, neutralized with alkali, coagulated by warming, dried, and the solvent extracted to give peat wax (m. 73–72 C) of improved quality; the yield is 12 per cent. Mother-liquors from the process may be treated for the recovery of the oxalic acid.

Composition and Constants of Peat Wax. In 1951 Reilly (and Mulcahy) reported that mona wax, or Highland peat wax, contains approximately 50 per cent of a complex bitumen material, 35 per cent of peat esters, and 15 per cent of resin. Processing produces waxes varying in color from dark brown to white and also causes changes in physical properties, which are

not advantageous. Mona wax is softer than montan wax, and 10 to 15 degrees (C) lower in melting point; it has a slightly higher dielectric strength and a slightly lower solvent-retention power.

The following are analytical constants on crude wax prepared by extracting with and then evaporating the solvent (petrolic ether) at a temperature below 30°C: acid value 66, saponification number 132.9, ester value 66.9, hydroxyl value (Witzöff) 50.2, and iodine number (Hübl) 39.4. After heating the crude wax in a nitrogen atmosphere at 80°C for 24 hours the hydroxyl value drops off sharply. The constants then are: acid value 60.7, saponification number 136.0, ester value 75.3, hydroxyl value 18.3, and iodine number 40.0[42].

It appears that on heating or lengthy storage of the crude wax, the OH groups of the hydroxy acids react with the COOH group, to form polyesters or estolides

$$x\ \mathrm{HO{-}R{-}COOH} \rightarrow \mathrm{HO{-}(R{-}COO)_{x-1}{-}R{-}COOH} + (x - 1)\ \mathrm{H_2O}$$

Peat wax (alcohol-vapor-extracted from peat) is easily soluble in amyl alcohol, less soluble in ethanol and methanol, and only partially soluble in ethyl ether and benzene, giving a dark green solution and leaving a dark brown residue. The crude wax may be separated by selective extraction with ether into soluble and insoluble portions. The soluble portion upon saponification with NaOH yields two alcohols and acids. The alcohols melt at 124–130°C; both correspond to the formula $C_{20}H_{40}O_4$ (m. wt. 344). The brown substance insoluble in ether melts at above 240°C and has the formula $C_{21}H_{35}O_7$ (m. wt. 399). The acid of the substance soluble in ether is green in color, softens at 145° and melts at 184°C. It has the formula $C_{15}H_{23}O_5$ (m. wt. 297). There exist other unidentified substances in peat wax.

Ryan and Dillon[35] describe the wax obtained by extraction from Irish peat as a yellow crystalline wax which melts at 76°C, is soluble in warm organic solvents, and has an acid value 73.3, saponification number 73.9, and iodine number 16.0. It contains 53 per cent of saponifiable matter. Its chief acid is montanic, which in its pure state melts at 83°C and has a mean neutralization value of 138.3. The unsaponifiables crystallize out from benzene to fine needles (m. 58–59°C, density (d^{15}) 0.920, and contain no appreciable amount of primary or secondary alchols.

Montanin Wax. Ryan also refers to a so-called *montanin wax* which apparently is a partially neutralized peat wax. Montanin wax melts at 95–97°C, is of a hard texture, and has a density (d^{15}) of 0.980, acid value 56.9, ester value 1.0, saponification number 57.9. It contains 41.3 per cent of montanic acid, 23.9 per cent of sodium montanate, and a remainder of unsaponifiables.

Montan Wax

Montan wax is commercially obtainable by the extraction of bituminous lignite or bituminous shale, by extracting it with a suitable solvent or solvent mixture. The latter is of an azeotropic type of nonpolar and polar solvents. The customary nonpolar solvent is benzene, and the polar solvent is alcohol. The crude wax so extracted is always blackish in color, and for most purposes must be deresinified. The four grades of montan wax in commerce are customarily designated as "crude," "deresinified," "yellow refined," and "white bleached." The last named is, however, not a true montana wax. No means has yet been found of fully bleaching montan wax without considerably altering its composition.

Meyerheim[20] has given the extremes of wax content in brown coals, to which the lignitic coals belong, as 1 to 27 per cent. The lower the degree of carbonization the higher the wax content. At Halle-Riebeck the customary recovery is 10 to 15 per cent, and occasionally runs have been obtained of an optimum of 18 per cent of wax. The crude wax contains largely long-chain esters, together with free wax alcohols, wax acids, and resinous and sulfur compounds (0.3–0.6 % S). The total acids, free and combined, amount to over 50 per cent.

Properties of Natural Montan Wax. Pschorr and Pfaff[27] have described the crude wax from the Riebeck Montan Works as having the following analytical constants: acid value 22.7, ester value 36.7, saponification number 59.4, and iodine number 13.9. Zöllner[49], however, gives the saponification number of crude montan wax as 74.4–75.5 by the older standard method, and 79.7–81.2 by the newer Hezel method (diethylene glycol as solvent). Meyerheim[20] gives the constants of the crude wax as follows: melting point (drop) 86°C, acid value 25, ester value 53, saponification number 78, iodine number 17.6, and unsaponifiable 36.4 per cent. The total wax acids, free and combined, amount to about 50 per cent, and melt at 82°C. The density (d^{15}) of montan wax is 1.02, whereas the paraffin wax refined from lignite tar is 1.02.

Marcusson and Lederer[18] gave the constituents and constants of two German crude montan waxes respectively as follows: resin 29, 29 per cent; brown coal dust 0.2, 0 per cent; alcohols 11, 6.7 per cent; normal wax acids 49.5, 52.3 per cent; hydroxy acids 3, 3 per cent; acids containing sulfur 6.5, 8 per cent; melting point 76–82°C, 76–82°C; acid value 27.8, 31.0; ester value 61, 61; saponification number 88.8, 92.

Properties of Deresinified Montan Wax. Ode and Selvig[23] reported the following constants for a Riebeck-brand of deresinified montan wax: melting point 82–83°C, acid value 24, saponification number 103, ester value 79, and resin (ethyl ether soluble) 14 per cent. These investigators state that Riebeck's so-called "deresinified wax" still contains 5–7 per cent of resin.

and the extracted "resin" about 60 per cent of wax and but 40 per cent of resin.

Montan wax is soluble in benzene, chloroform, carbon tetrachloride, trichloroethylene, and hot benzin; it is incompletely soluble in hot ethyl ether or in boiling water.

Processes of Extraction of Montan Wax from Lignite. Crude montan wax is obtained from lignite (brown coal) by extracting it with a suitable solvent. The lignite is crushed or granulated and dried to a 10–12 per cent moisture content. The granules are then sieved to remove powder therefrom, and the powder-free granules are extracted with a mixture containing about 85 per cent benzene and 15 per cent unrefined wood alcohol containing methyl and isopropyl alcohols. This extraction is normally carried out at 90–100°C. The alcohols dissolve the cell walls of the brown coal granules and free the wax therefrom, thereby enabling the wax to be dissolved by the benzene. The wax solution is separated, and the solvent distilled off, leaving the crude montan wax as a residue. The crude montan wax is dark colored and contains resinous and asphaltic impurities. The yield of wax is 10–18 per cent. The process used today is essentially the same as that advocated by von Boyen in 1901; the practice of granulating, drying, and extracting the wax is followed by at least six different works in Germany. The residue wax is briquetted for utilization as a fuel. Marcusson and Smelkus found that an increased yield of crude wax could be obtained by employing a temperature of 260°C and 5 atmospheres pressure, but then the residue cannot be briquetted, and the crude is somewhat too resinous.

The only process in which the bituminous lignite is treated in the natural damp state in which it is hauled from the mine, is that of Frank and Ziegler, known as the "wet extraction process." One part of crude alcohol is added to four parts of benzene, as a solvent to facilitate extraction and improve the yield. Thüringian lignite, when treated with benzene alone at 260°C and six atmospheres pressure, yields a crude bituminous wax which is brown or black in color.

Most of the crude montan wax produced at the montan works in Germany was subjected to a process of refining to rid it of the objectionable resinous and asphaltic impurities as far as was economically possible (see Purification and Refining of Montan Wax). The production of the montan waxes at the Riebeck Works in Germany was rated at 36,000,000 pounds per year before the advent of World War II. Of this amount the United States imported closed to 7,000,000 pounds in 1939, after which importations dropped off precipitously. Importations were reinstated in 1949, but in greatly reduced volume.

Purification and Refining of Montan Wax. The crude montan waxes are somewhat limited in their utility because of their dark color. In order

to use them in the manufacture of esterified waxes, it is necessary to remove the excessive amount of resinous and asphaltic matters, and also to lighten the color. It was customary at the Riebeck Montan Works (A. Riebecksche Montanwerke, A. G., Halle, Germany), to deresinify the crude wax at one of their several plants. A portion of their output of crude wax extracted at Halle Riebeck was deresinified by a simple solvent (methanol) treatment, to produce a semirefined montan wax; but as a step further much semirefined wax was shipped to Gersthofen for further purification to lighten its color and to produce certain ester waxes (also see German I. G. Wax Process, p. 459). Crude montan wax is now shipped from the Russian Occupied Zone to Gersthofen for refining under a reciprocal trade agreement to return in exchange a specified proportion of esterified or refined waxes, prepared from the crude.

Various methods have been proposed and used to produce a montan wax of sufficiently light color to enable its use in those instances where light color is required. Strong acids have generally been used to refine the wax, although strong alkalies have also been employed. Distillation at low pressures produces a light-colored wax, but of altered composition. Selective solvents are also used as a means of purification of the semirefined wax. Although the various methods of bleaching result in a product of light color, the bleached waxes so produced tend to crystallize under certain conditions of use, ostensibly because of their high content of free wax acids of high molecular weight (26 to 29 carbon atoms).

Stickdorn Acid Process. For the production of a light yellow montan wax, Stickdorn[40] in 1939 described a process in which the crude wax is purified and refined by treating it at an elevated temperature (100–150°C) with a sulfuric acid purifying agent in a quantity amounting to at least one-quarter of its weight of the wax treated; thus making it possible by further refinement to separate the wax from the impurities present. The procedure is to melt the crude wax, raise the temperature above the melting point, and add the acid while stirring the mass vigorously at a temperature preferably between 130 and 150°C, until the desired purification is complete; this operation usually takes from 4 to 8 hours. The sulfuric purifying agent, according to the Stickdorn patent, may be concentrated sulfuric acid, its monohydrate, fuming sulfuirc, or chlorosulfonic acid, and acid compounds, such as alkali metal bisulfates. Von Boyen[45] employed a mixture of concentrated nitric acid 10–20 parts and sulfuric acid 90–80 parts.

In the Stickdorn process the acid treatment transforms the montan wax into a paste-like material which is then mixed with water, washed with additional water, and neutralized by the addition of a little alkali to the wash water. The washed and neutralized wax is then dried, and separated from its impurities by mixing it with decahydronaphthalene or heavy benzin

and brought to a boil. Thereafter the wax is filtered from the coal-like pulverulent residue and subjected to distillation *in vacuo* for removal of solvent. An alternative method to distilling off the solvent is to precipitate the wax by a chilling operation, when it may be removed by a centrifuge or by the addition of a suitable solvent. The end result is a light yellow wax, having an acid number of 120 and a melting point of 80°C.

Stickdorn Alkali Process[40]. Montan wax, according to Stickdorn, can also be purified by treating it with caustic alkali at a temperature at which the wax is in a molten condition; the treatment is continued until the alcohols of the wax are converted into the corresponding acids. This supplemental treatment may be effected either before or after the acid treatment. In carrying out this treatment 100 parts of raw montan wax are heated in an autoclave with 17 parts of sodium hydroxide and stirred for a period of several hours at 290°C during which heating the hydrogen and water vapor evolved are continuously blown off. The hard dry mass is then further treated at 125°C by slowly adding 1000 parts of concentrated sulfuric acid, after which the mixture is heated to 150°C for five hours, and at a temperature of 180°C for three hours. Thereafter the mass obtained is treated by the procedure first described above as to washing and separating the wax. By the "caustic-soda autoclave process" described, about 65 parts of yellow montan are obtained per hundred pounds of crude. The refined wax has an acid value of 128 and a melting point of 81°C. Yellow montan waxes of the kind just described are not so well suited for direct use in the arts and industries, but are utilized in the production of products (Gersthofen waxes) of their esterifications, or etherification, and the like. (Also see "I. G. Waxes," p. 457).

Romins'kii[43] refined detarred lignite (montana) wax by oxidation with 120 per cent by weight of chromic acid anhydride in the presence of 42 per cent sufuric acid, employing three stages of operation; the wax so treated is washed with sulfuric acid (42%), and then with boiling water to remove the acid. The yield of refined product was 80 per cent by weight of the detarred wax. The refining process, however, partially decomposed the esters, oxidized portions of the nonsaponifiable matter, and formed an increased amount of the higher wax acids. In order to avoid decomposition of the wax esters Romins'kii bleached detarred wax with 400–500 per cent by weight of activated carbon. The yield, however, did not exceed 52 per cent; the refined product was clearer, the color somewhat improved, and the acid content lower than the original wax. It was found that wax which had been previously treated with chromic anhydride can be bleached by energetic stirring of the wax with 10–20 per cent by weight of activated carbon at a temperature of 110–115°C for about 45 minutes.

Raw lignite wax (Alexandrian) contains 24.5 per cent of tar, 1.9 per cent ash, and 5.4 per cent of benzene-insoluble material. The wax extracted from the lignite with benzene can be detarred with ethyl acetate or with benzene-acetone solution (1:3). The extracts are chilled to about −7 to

−10°C and filtered. The yields of chilled wax are slightly above 2 per cent, while the yields of detarred wax are about 70 per cent. The extraction of the lignite should be at high temperatures but the detarring conducted at low temperatures, since the solubility of the tar diminishes with a rise in temperature.

Semi- and Fully Bleached Montan Waxes. The designation "fully bleached" as applied to montan wax implies that the crude has been refined to the extent that its composition has been considerably altered. Either the commercial white product consists mostly of montanic acid or contains a considerable amount of ceresin. To prepare the wax from the crude the first step is to distil it with superheated steam at 250°C. The resultant semi-refined wax is yellow in color, lustrous, somewhat brittle, and has a melting point of 75°C. The loss on distillation is attributed to decomposition of the resin and sulfur compounds, splitting of wax esters into free fatty acids and unsaturated hydrocarbons, and formation of ketones and of pitchy residues. The steam-distilled wax can be further purified by treating it with a sulfuric acid purifying agent, such as potassium chromate and sulfuric acid, and finally by treatment with activated carbon. Purification by solvent such as benzene, and pressing and bleaching have also been resorted to. The actual yield of the white wax may be as low as 30 per cent, on the crude basis. Crude wax is strongly optically active whereas the distilled or refined waxes are inactive.

Yellowish-white montan wax of a crystalline structure was described as early as 1920 by Eisenreich[7]. He relates that such a wax was used for candlemaking in Schliemann's factory at Hamburg. Whether this was a distilled and acid-refined product has not been stated. It had a melting point of 77°C, acid value 93.0, saponification number 94.6, ester value 1.9, iodine number 12.0 (Wijs), acetyl acid number 93.0 unsaponifiable matter, 29.1 per cent; acetyl value 11.8. Eisenreich identified the predominant acid in the wax as one having the formula, $C_{29}H_{58}O_2$, and a melting point of 82.5° as earlier established by Hell. It is quite certain that the C_{29} acid is not *normal*-montanic acid (m. 90.3°C). It might possibly be 27-methyloctacosanoic acid (m. 84.4°C).

For the production of bleached montan wax, Pungs and Jahrstorfer[28] in 1932 suggested that the wax be first saponified and the resulting fatty acids and alcohols separated. The alcohols are then bleached by a solid absorbent, such as activated carbon, and the acids separately treated with an oxidizing agent, namely a solution of potassium chromate and sulfuric acid. The bleached substances are then re-esterified, and by adding other alcohols and acids, the desirable properties of the wax may be enhanced. This proposal laid the foundation for the development of synthetic waxes known as the "I. G. Waxes" (see p. 457). No method has been evolved whereby montan

wax can be fully bleached without considerably altering the original ester composition.

The distilled and refined wax, which is of light color, has the following analytical constants: melting point (drop) 77°C, acid value 82.7, ester value 7.6, saponification number 89, iodine number 10.9, montanic acids content 62.6 per cent, unsaponifiable 37.3 per cent. It has a penetration value (# 14 Needle-5 sec/100 g/25°C) of 9½–10, and is a trifle harder than white beeswax.

Breuer and Zentmyer[2] bleached montan wax by heating with sulfuric acid and treating the emulsion thus produced with a mixture of sulfuric-chromic acids, or with anhydrous chromic acid alone. In this method the bleached wax is first treated with a glycol to partially esterify the monocarboxylic acids and to convert most of the dibasic acids to monoesters. It is then re-esterified with a higher polyhydric alcohol, i.e., pentaerythritol, whereby the resulting wax shows a hardness about equal to carnauba wax and is free from gelled products.

A pure white wax, known as *montanilla wax*, is prepared by bleaching a mixture of paraffin wax and deresinified montan wax. It has a comparatively low saponification value, 23.3–23.6 (Hezel method).

Ultimate Composition of Montana Waxes. Montana waxes are generally recognized as waxes extracted from lignites found in many parts of the world. These waxes, according to their origin, differ somewhat in the proportional make-up of the constituents. *Peat wax* is a variant of lignite montan wax. The term *montan* in its restricted sense applies to the particular extraction of Central Germany lignite. The term *montana* is used here in the broader sense. All montana waxes are mixtures of monohydric alcohol esters and high molecular weight acids, accompanied in varying degrees by bituminous resin and asphaltic material. Various commercial processes employed to free a montana wax from asphaltic material and lighten its color, tend also to alter the chemical composition, by decreasing the amount of monohydric alcohol esters and increasing the amount of wax acids and hydrocarbons.

Ode and Selvig[23] have made a study of the ultimate composition of German, Czechoslovakian, and American montana waxes, and obtained the following range of analyses on a dry basis: ash 0.1 to 0.3 per cent, hydrogen 10.6–12.6 per cent, carbon 77.3–80.2 per cent, nitrogen 0.0–0.3 per cent, sulfur 0.3–0.6 per cent, oxygen (by difference) 6.8–10.4 per cent. The Riebeck brand shows ash 0.3, hydrogen 12.6, carbon 79.7, nitrogen 0.0, sulfur 0.6, and oxygen 6.8 per cent.

The monohydric alcohol esters are composed of C_{20}, C_{22}, C_{24}, C_{26}, C_{28}, and C_{30} alcohols, combined with C_{20}, C_{22}, C_{24}, C_{26}, C_{28}, and C_{30} acids. The American montana waxes covered by these investigators include those

derived from lignites of Hot Spring County, Arkansas, and Amador County, California; also a commercial brand known as "American Montan Wax C."

Chemical Composition of Montan Wax. Crude montan wax is essentially a mixture of wax esters, free wax acids, and resin accompanied by a very small amount of asphalt. Since the resin, inclusive of the asphalt, is the undesirable constituent, the crude wax must be purified to a more or less resin-free wax to make it suitable for commerce. The refined wax contains about 66 per cent of esters, 23 per cent of wax acids in the C_{25}–C_{31} range, and a minor amount of free alcohols, ketones, and resin not entirely removed by ordinary purification.

Upon saponification the crude wax will, according to Meyerheim[20] (1919), yield about 50 per cent of wax acids (m. 82°C). This investigator referred to the lower acids as C_{20}, C_{22}, and C_{24}, which in part are combined with C_{20}–C_{26} alcohols. In 1930 Holde and Bleyberg[13], who employed the modern technique of micro-distillation and x-ray analysis, established with certainty that these wax acids do have a chain length of an even number of carbons. They claimed to have isolated a normal C_{28} acid (m. 89°C), and indicated the presence of a normal C_{26} acid (m. 85.9°C). Prior to that time it was generally believed that the principal constituent of montan wax was a C_{29} acid (m. 84°C), which became known as *montanic acid*, in reality comparable with *isononacosanoic acid*.

In 1922 Tropsch and Kreutzer[44] esterified crude montanic acid with methanol and separated the esters by fractional distillation. A fraction (b_5 265–267.5°C) contained an acid $C_{27}H_{54}O_2$ (m. 82°C), and a fraction (b_5 277.5°C) contained an acid $C_{29}H_{58}O_2$ (m. 86–86.5°C). The C_{27} acid they named *carboceric acid*, in reality comparable with *isoheptacosanoic acid*. The C_{29} acid they stated was true montanic acid. The C_{29} acid (m. 86.8°C) was termed *geoceric acid* by Brückner to distinguish it from a normal chain wax acid. A little later Tropsch and Kreutzer[44] reported the isolation of a C_{25} acid (m. 78°C?), which ostensibly corresponds to *isopentacosanoic acid*. *Melissic acid*, C_{31} (m. 90°C), has also been reported as a minor constituent of montan wax. In melting point it is identical to *isohentriacontanoic acid*. It is of interest to note that the melting points of these so-called *odd* carbon wax acids appear to be identical to synthetic *iso*-acids, which have chain lengths of an even number of carbons with a methyl side chain linkage, namely *iso*-C_{25} (m. 77.6°C); *iso*-C_{27} (m. 82.5°C); *iso*-C_{29} (m. 86°C); and *iso*-C_{31} (m. 90°C).

Pschorr and Pfaff[27] in 1920 identified in the ether extract of crude montan wax from Riebeck Montan Works (Germany) an acid of molecular weight of 426 and melting point 83.5°C. (This corresponds to a mixture of *isocerotic acid* with a minor amount of *isomontanic acid*.) The acid was pre-

pared also by saponifying a subsequent acetone extraction, treating the calcium salts of the saponified extractions with hydrochloric acid, and then converting the acid to the ethyl ester (m. 66.5°C) from which it can be isolated in the pure state. (The melting point of the synthetic ethyl ester of a C_{29} wax acid is 66.6°C, whereas that of the ethyl ester of the C_{28} acid is 64.6°C.) Hence reasonable proof exists that the *free* montanic acid (Brückner's *geoceric acid*) of montan wax is a C_{29} acid even though the monoester constituent may contain *n*-C_{28} acid. Eisenreich[7], Hell, and others were convinced of the presence of the C_{29} acid (m. 81.5–83°C) as the principal constituent, associated with minor amounts of its homologs.

Pschorr and Pfaff[27] identified in the ether extract of crude montan wax (35%) the alcohol, *tetracosanol*, $C_{24}H_{50}O$. A subsequent acetone extraction (12.5%) yielded *hexacosanol*, $C_{26}H_{50}O$. The residue (48%) was rich in esters, from which upon saponification three alcohols, *octacosanol* (C_{28}, m. 83°C), hexacosanol (C_{26}, m. 79°C), and triacontanol (C_{30}, m. 88°C), were isolated. They identified a resin in the ether extract of the crude wax. This resin had a saponification number of 0, an iodine number of 54, and crystallized in prisms (m. 241°C). They gave the resin alcohol the formula $C_{24}H_{34}O_2$.

Tropsch and Kreutzer[44] found about 4.7 per cent of an acid having the formula $C_{31}H_{62}O_2$ in the total acids of montan wax. (This acid is usually in the uncombined state.) The chief wax acids of the esters of montan wax, it is generally believed, are acids with an even number of carbons, regardless of whether they are *normal* or *iso* acids. The thallous salts of the montan wax acids C_{28}–C_{29} have a branched chain, according to the transition changes, when melted, obtained with the crystalline-liquid (c-l) phases as studied by Walter[46], changes which were in contrast with those noted in the behavior of the C_{26} cerotate and other esters having a normal chain.

Uses of Montan Wax. Montan wax has been of great importance in its industrial applications, that is, for electrical insulation, for wax coatings on leather, for shoe polish pastes, for brewers pitch, etc. It has been used in carbon paper dopes, belt dressings, cables, precision casting, dry cell batteries, rubber manufacture, phonograph records, explosives and fuses, wire drawing, and in general wax compounding. *Double-refined montan wax* is of particular value in making polish pastes, since it is hard, has good binding power and good solvent retention, produces a superior gloss, and gives a mirror surface to the polish. It blends well with carnauba, candelilla, and other hard waxes used in polish formulations. Montan wax was at one time extensively employed for interleafing sheets, which are used in dry mounting photographs. Crude montan wax may be advantageously utilized to lower or depress the pour point of oil, and is used in lubricating greases. Large tonnages of crude montan wax are used in Germany for the manu-

TABLE 65. APPROXIMATE COMPOSITION OF CRUDE MONTAN WAX FROM CENTRAL GERMANY

Esters of Wax Acids:	53%
Tetracosyl esters of C_{26}–C_{34} acids	
Hexacosyl esters of C_{24} and C_{28} acids, 3–4%	
Octacosyl esters of C_{26} and C_{28} acids	
Tricontanyl esters of C_{28} and C_{30} acids, 32%	
Hydroxy acid esters, 12–14%	
(e.g., $C_{27}H_{54}(OH)CO \cdot OC_{28}H_{57}$ (m. 93°C)	
Free Wax Acids: (m. 81.5–83°C)	17%
Isotricosanoic (C_{23}, m. 77°C)	
Isopentacosanoic (C_{25}, m. 77.6°C)[c]	
Isoheptacosanoic (C_{27}, m. 82.5°C), 1–2%[c]	
Isononacosanoic (C_{29}, m. 86°C), 8%[b]	
Isohentriacontanoic (C_{31}, m. 90°C), 4.5%[c]	
Free Alcohols:	1–2%
Tetracosanol, $C_{24}H_{50}O$ (P & P)[a]	
Hexacosanol $C_{26}H_{54}O$ (P & P)[a]	
Ketones:	3–6%
Cerotone, $(C_{25}H_{51})_2CO$, m. 94°C	
Montanone, $(C_{27}H_{55})_2CO$, m. 95.8°C	
Resin	20–23%
$C_{30}H_{60}O$ and other resin alcohols	
$C_{34}H_{34}O_{21}$, montan resin (m. 241°C, I no. 54)[a]	
$C_{42}H_{84}O$ (m. 63.5°C)	
Sulfur-containing hydroxyacid esters, 4–5%[d]	
Sulfur-containing acid resins, 6.5–8%	
Asphaltic Material:	3%

[a] Pschorr and Pfaff[37]; [b] F. v. Brückner's geoceric acid; [c] Eisenreich[7]; [d] Smelkus[38]; [e] Tropsch and Kreutzer[44].

Note: Although the esters are listed above as alcohols combined with carboxylic acids having an even number of carbons, it is quite possible that the alcohols may be combined with *iso*-acids having an odd number of carbons.

facture of synthetic waxes of high molecular weight; the wax acid constituent is amenable to esterification in many ways to yield waxes of unique and valuable properties. (See "I.G. Wax" and "Gersthofen Wax".)

Montan Wax Sulfonic Acids. These derivatives of montan wax have tanning properties; their alkali metal salts are useful as washing and wetting agents, and their heavy metal salts are useful as pesticides. The sulfonic acids are prepared by heating montan wax sulfonyl chlorides with water which causes them to hydrolyse. The sulfonyl chlorides are prepared by treating bleached montan wax with a mixture of chlorine and sulfur dioxide (mol ratio 1 to 1) under the influence of active light, or in the presence of solvents or catalysts such as peroxides. [Heisel, P., and Lech-Chemie Gersthofen, German Patents 817,307 and 822,687 (1951).]

Czechoslovakian Montan Wax. Because of the inavailability of montan wax from Germany following World War II, a relatively small amount of montan wax was imported by the United States from Czechoslovakia.

A brown coal from the Josef Jan mine at Pila, near Karlovy Vary (Karlsbad) Czechoslovakia, is extracted by benzene. Machek[16] states that the extraction is carried out on a wax coal which is granulated to 8–10 mm size, and contains 10–15 per cent moisture. Ode and Selvig[23], who have analysed the Czechoslovakian montan wax, report its characteristics: melting point 73–75°C, acid value 36, saponification value 89, ester value 53, resin 45 per cent, and asphaltic material 5 per cent. It has about twice the resin content of the Riebeck (German) brand of crude montan wax and almost twice as much asphaltic material. The crude is about as resinous as Californian crude montan wax, and is not completely miscible with paraffin as is the semifluid wax from California lignite. Ode and Selvig[23] give the ultimate composition of Czechoslovakian montan wax on a percentage dry basis, as follows: ash 0.4, hydrogen 11.7, carbon 79.2, nitrogen 0.2, sulfur 0.3, and oxygen (by difference) 8.2 per cent.

Polish Montan Wax. Montan wax is produced on commercial scale from Polish peat with a yield of 8–17 per cent. The crude wax melts at 81–83°C; its acid value is 40–43, ester value 25–29, and saponification number 65–72. It is soluble in ether to the extent of 35–37 per cent. It has a specific gravity (d^{25}) 1.030, ash 1.1–0.5 per cent, and benzene insoluble 0.1 per cent. By extraction with alcohol five fractions were obtained: soft resin 6.5; resin (m. 67–68°) 6.5; wax contaminated with resins 32; pure wax (m. 82–84°C) 15; and asphalt residue 40 per cent[29].

American Montan Wax. A suitable substitute for the montan wax extracted from the lignites of Saxony and Thüringia is to be had in the dark, hard, and odorless ester wax extract so-called montana wax from certain American lignitic coals found in the "Northern Great Plains Province" [3] which includes western North Dakota, eastern Montana, and northwestern South Dakota, and extends into Canada. The most important lignite deposits in the "Pacific Coast Province" occur in Amador County, California. There are deposits in the "Gulf Province" but they are lenticular ones of limited lateral extent.

Although higher yields of wax are obtainable from the American lignites with a solvent mixture of benzene and alcohol than with benzene alone, the properties of the benzene extract more closely resemble the commercial grades of the German montan wax. According to a survey made in 1945 by the U. S. Bureau of Mines the highest yields of wax are obtainable from certain Arkansas and California lignites. Small quantities of extractable wax are obtainable from the lignitic coals of Montana, North Dakota, Texas, and Washington.

The American Lignite Products Company operates a plant at Buena Vista, California, for extracting the montana wax (*American montan wax*) from California lignite mined in Amador County. The lignite for the plant

is strip mined from a bed near Ione. The wax has a melting point comparable with the Riebeck brand deresinified montan wax (m. 81–85°C). The yield of wax from Amador County lignitic coal is 6.6–7.1 per cent on the air dried coal basis, when benzene is employed as a solvent, and 9.5–11.1 per cent when using a benzene-alcohol mixture[23]. Similar high yields are obtainable with Arkansas lignitic coal. The yields of benzene extract from similar coals in other states are less than 2 per cent.

American montan wax when extracted from lignitic coal by benzene has an acid value which ranges from 36 to 46, a saponification number of 81 to 112, and an ester value between 41 and 68. It contains 48 to 68 per cent resin, and 3 to 7 per cent asphalt. A commercial brand known as "American Montan Wax C" showed the following constants: melting point 77–81°C; acid value 38, saponification number 105, ester value 67, resin 24 per cent, asphaltic material 5 per cent. It is less resinous than Czechoslovakian montana wax, and compares favorably with the Riebeck brand of crude montan wax, although it has a little more asphaltic constituent.

An improved grade of American montan wax, known as "Alpco Wax Type 16" of the American Lignite Products Company, Ione, California, is reported to have the following characteristics: melting point (ASTM, D–27–49) 85–87°C (185–189°F); acid value 50–55; saponification number 112–120; color brownish black; resin 21–24 per cent; asphaltic matter 3.3–3.8 per cent; ash 0.1–0.4 per cent; specific gravity (d^{25}) 1.020–1.030; fracture, conchoidal; completely soluble in hot benzene and in hot methyl ketone. Its ultimate analysis is ash 0.2, hydrogen 12.2, carbon 79.4, nitrogen 0.0, sulfur 0.3, and oxygen (by difference) 7.9 per cent.

The prices of American montan waxes range between 25 and 31 cents per pound, depending upon the type of wax and the quantity ordered. They are packed in 6-ply multiwall paper bags, 100 pound net.

Devonshire Lignite Montana Wax

A suitable substitute for the montan wax extracted from the lignites of Saxony and Thüringia is found in the dark, hard, and odorless ester wax extracted from Devonshire lignite. The wax may be extracted with benzene. It has a melting point of 69–84°C, and is of harder texture than similar waxes extracted from the various English and Scottish peats. The wax has an acid value of 29–34, saponification number 70–77, and ester value 36–45. It contains about 40 per cent of resinous material which could be removed by ethyl acetate extraction at −10°C.

The crude wax may be refined by treating the dark-brown resin-free wax with chromic and sulfuric acids, followed by fuller's earth, whence a light-yellow hard wax (m. 82–86°C) may be obtained. The refined wax has an acid value of about 73, and a saponification number of about 130. It

was found by Cawley and King[4] that extraction at 250°C and 35 atmospheres pressure will give increased yields, but the wax is softer and of lower melting point, namely 58–68°C.

Valuable resins and waxes have been extracted from specimens of lignites from Australia, Borneo, Nigeria, and Pakistan. As much as 15 to 25 per cent of extractive is obtainable from Nigerian lignite.

Extraction of the lignite from Neyveli in South Arcot, India with benzene, or better, toluene, yields 40–60 per cent of a waxy substance (m. 73–74°C), which has a density of 1.0400, acid value 34, and saponification number 80, and is similar in properties to crude montan wax. The South Indian extractive substance consists of 50 per cent ether-soluble resins and 50 per cent of ether-insoluble "montan wax." The lignite residue can be used as a fuel.

Wax from Nonlignitic Coal

Coal and other solid carbonaceous materials can be extracted with benzene, ethanol, tetrahydronaphthalene, etc., with or without the addition of hydrogen, under pressure. The extraction products, after removal of ash, undecomposed coal, and part of the extracting agent, are mechanically separated into a wax fraction and an asphalt fraction either by sedimentation or centrifuging. The asphalt fraction may be blown with air and used as a road asphalt or hydrogenated to form a fuel oil. The wax fraction is treated with selective solvents; the purified product is used for wax-containing compositions, for oxidation treatment, or, by hydrogenation, is converted into lubricating oils. The working-up of coal extracts has been conducted by the I.G. Farbenindustrie A. G.

Upper Carboniferous coals from Western Australia, such as the Collie coal field laid down during Early Permian times, contain wax. Such coal is subbituminous and noncoking, and contains 15 to 30 per cent moisture. When extracted with boiling benzene it yields up to 0.5 per cent of a brown wax. Then with a boiling mixture of equal volumes of benzene and alcohol it yields up to 3.5 per cent of a brown-black brittle resinous solid.

LIGNITE PARAFFIN WAXES

Saturated hydrocarbons, or alkanes, are obtained in the pyrogenetic decomposition, or destructive distillation, of lignitic brown coal. The wax-bearing distillates (kerogens) from German brown coal are refrigerated, admixed with diluent, filtered, and the slack wax thus obtained is sweated out to remove the entrained oil; the *refined paraffin wax* has an average composition of $C_{28}H_{54}$.

The English, Rhenish, Westphalian, and particularly "Oedingian leaf" shales yield paraffins. "Bituminous shales" in Sicily, Sweden, Esthonia,

and Serbia yield burning, intermediate and lube oils, and a considerable amount of "paraffin scale," both hard and soft. Crude shale oil made by retorting Colorado Green River oil shale yields paraffin waxes.

Refining of Lignite Paraffines

Bituminous lignite has been used for many years as a material for the dry-distillation process and the working up of the resultant lignite tar into mineral oils and paraffin wax, particularly in the Saxon-Thüringian district. The distillation of lignite tar is conducted at about 650°C in a manner best suited to separating oil as free as possible from paraffin wax, and concentrating the wax in the paraffin masses[36]. To do this, the chemically treated crude oil is distilled into one or two fractions and a paraffin mass, and the separation of the oil and mass takes place as soon as the distillate is congealed by refrigeration. The first oil distilled contains the lighter ends such as lignite-tar benzin, solar oil, and pale heavy oil, as well as the solar paraffin mass.

The solar paraffin mass on pressing yields "solar-paraffin scale" and a gas oil which is marketable. The principal paraffin mass of the tar yields another "paraffin A-scale" and the filter oil which on distillation, not to dryness, yields crude oil and paraffin mass B from which on distillation is obtained filter oil and "B-scale." B-scale is distilled to red oil and paraffin mass C which can be worked up into "filter oil heavy" and "C-scale." A-scale is a hard paraffin mass, and B- and C-scales are the softer masses, which are crystallized out at a lower temperature. These paraffin masses are worked up to furnish the *refined paraffines* much in the same way as some petroleum paraffines are handled. There are, of course, many possible variations in the process described above.

The following are melting points of crude paraffines or scale waxes: "A-mass" 50–55°C; "B-mass" 40–45°C; "C-mass" 38–42°C; "solar mass" 35–40°C. In the refining, the paraffin masses are first crushed in a mechanical crusher; the pulpy mass is drawn by a pump and delivered to the filter press, where the crystals of paraffin wax are separated from the oil. The filter press is the filter plate type. The paraffine cakes are scraped from the cloths of the plates by wooden knives. The press cake contains oil and is then transferred to a vertical press and subjected to a pressure of 100–150 atmospheres to press out the oil. The press cake is subjected to further treatment with crude benzin and direct steam heat in the melting vessel. When the mixture of wax and benzin is poured into water the paraffine solidifies. Then when the scale is pressed in a hydraulic press, the benzin, which is a lignite tar distillate, carries away with it the heavy oil adhering to the scale. To refine the paraffine the process is repeated twice, that is, the scale receives two pressings. Scottish paraffin wax, however, has a more crystalline structure than that of Saxony Thüringian, and is recovered admirably by sweating, requiring no benzin washing

Refined paraffine that has been washed as described would still contain

traces of benzin. The paraffine to be fully refined must be placed in a retort or cylindrical vessel, warmed by means of steam, and the benzin swept out by the action of a steam jet placed under the vessel. After the paraffine has been rendered inodorous by steaming, it is faintly greenish yellow in color—not pure white—and must be treated with decolorizing agents such as animal charcoal, ferrocyanide residues, clay, or a mixture of pure carbon and silicate, preferably the latter. The decolorizing agent must be anhydrous, or made so: 1 to 2 per cent of the dry powder is added to the melted paraffine, and mechanically mixed in the vessel which is heated to 70–80°C by steam. The filtering can be done through paper, and with the same type of equipment used in pressing petroleum paraffin wax.

In crystallizing lignite paraffine, cooling is effected in shallow vessels by means of air, but the soft masses are further cooled with refrigerating brine in a manner similar to the handling of petroleum paraffin waxes.

The grades of refined lignite paraffine range in melting point from 35° to 62°C. Grades melting below 50°C (122°F) are classed as *soft paraffine*. Paraffin wax from lignite ignites at 160–165°C and volatilizes at 350–400°C. The density of lignite paraffine rises with the rise in melting point; e.g., 0.883 for paraffine m. 45°C, 0.908 for that m. 51°C, and 0.915 for that m. 58°C, the densities being determined at 20°C. The specific heat of lignite paraffin wax is 0.683.

Lignite paraffin scale m. 35–40°C (95–104°F) is used mainly in the manufacture of matches; that is, for impregnating match sticks. According to Egan and Mills[6], in making candle material paraffin scale wax can be mixed with a split fatty acid of an oil hydrogenated to an iodine number of 5 or less.

Lignite tar distillates are obtainable from many sources of bituminous lignites and shales found all over the world. Some are richer in wax than others. In the United States there is a black lignite in the state of Washington that has been found to produce 108 pounds of tar per ton. The tar on redistillation gave approximately 26 parts of light oil, 29 parts of middle oil, 7 parts of *paraffin wax*, 39 parts of heavy oil, 4400 cubic feet of gas, and the coke left in the still. The tars of French and Scotch shales are also reported to yield a considerable amount of wax.

Paraffin Wax from Scottish Shale Oil

The steps in the refining of wax from Scottish crude oils are: (a) distillation to separate the wax distillate fraction, (b) dilution of the wax distillate with a wax-free fraction, (c) extraction, (d) chemical treatment, (e) sweating, and (f) decolorization of the waxes. The wax distillate is controlled to have a final boiling point of 328°C at 40 mm pressure. The viscosity of the wax distillate is lowered and the wax content reduced from 28

to 18.5 per cent by dilution with a lower-boiling wax-free distillate. This blend is dewaxed by chilling and filtering, first at 38–40°F and then at 18–20°F. These waxes are treated with 96 per cent sulfuric acid at 130–140°F, neutralized with soda ash, and washed with water. The treating period approximates 30 minutes. Thorough water washing is necessary for satisfactory sweating. The waxes are further separated into different grades in the sweating plant. The oil discharged from the sweating plant contains about 48 per cent wax. The sweated waxes range between 100–105°F to 130–135°F setting point. They are decolorized by percolation through Florida clay.

Paraffin Waxes from American Shale Oil

A potential source of wax of sapropelic origin is available from oil-shale processing to supplement petroleum waxes in meeting the future market demand, as very large reserves of oil shale occur in Colorado, Wyoming, and Utah, according to a Bureau of Mines Report of Investigations (No. 4708). Crude shale oil made by retorting Colorado Green River oil shale when fractionated yields two principal wax-bearing fractions, namely "shale oil wax distillate," and the residuum from this distillation, which contains high melting point *paraffin wax*. The crude shale oil was produced by a batch process in an internally fired N-T-U retort at the Bureau of Mines Oil-Shale Demonstration Plant, Rifle, Colorado.

Tisot and Horne[43] have reported on the comparative efficiency of various dewaxing solvents. The preferred solvent is methyl ethyl ketone. The solvent process is most effective when the wax separates from an oil-solvent-solution in large, well-defined crystals, as it does with shale-oil wax distillate. The quantity of wax recovered at 32°F was 18.8 per cent of the wax distillate, or 6.6 per cent of the crude shale oil.

The procedure in dewaxing is either (a) to chill the wax distillate and solvent separately to dewaxing temperature (32°F or below), mix thoroughly, and filter; or (b) to mix the wax distillate and solvent, warm until complete solution is effected, and then chill and filter. The latter procedure yields a cake of well-defined crystals which is easily washed. The use of benzene or of ethylene dichloride with the methyl ethyl ketone held no marked advantage, nor did the lower dewaxing temperatures. The wax yield was 18.5, 21.6, and 22.6 per cent for dewaxing temperatures of 32°, 0°, and −20°F, but the increased yields at the lower temperatures did not appear economical because of the higher costs in lowering to such temperatures.

German Brown Coal Paraffin Wax

Paraffin wax is obtained by destructive distillation of German brown coal. The wax-bearing distillates are refrigerated, admixed with a diluent,

and filtered; the slack wax thus obtained is sweated out to remove the entrained oil. The refined paraffin wax has an average composition of $C_{26}H_{54}$. In the sweating and pressing operations the paraffine is separated from the paraffin oils by introducing into the mixture certain disc-formed cooling elements, from which the separated paraffine is continuously removed by scraping the stirring device to secure the greatest possible cooling action. This method was taught by Porges and Neumann[25], and is used today in principle by American refiners of petroleum paraffines.

It is reported that a specimen of the brown coal paraffin wax contained no more than 10 per cent of isoparaffins, which possess the mean formula $C_{22}H_{46}$. Naphthenic hydrocarbons C_nH_{2n+1}, C_nH_{2n}, C_nH_{2n-2}, and C_nH_{2n-3} have been found in waxes melting at 76°, 63°, 57°, and 50°C respectively.

References

1. Bardwell, C., *et al.*, *Trans. Utah Acad. Sci.*, **1**, 78–95 (1918); [*Chem. Abstracts*, **13**, 824 (1919)].
2. Breuer, F. W., and Zentmyer, D. T., U. S. Patent 2,586,780 (1952).
3. Campbell, M. R., *U. S. Geological Survey, Profess. Paper* **100** (1929).
4. Cawley, C. M., and King, J. G., *J. Soc. Chem. Ind*, **64**, 237–242 (1945)
5. Ciusa, R., *et al. Gazz. chim. ital.*, **51**, I, 55–60 (1921); *ibid.*, **52**, I, 125–128, 135–136 (1922).
6. Egan, J., and Mills, V., U. S. Patent 1,935,946 (1933).
7. Eisenreich, K., (Technical High School, Dresden), *Chem. Rev. Fett- Harz-Ind.*, **16**, 211–213 (1909).
8. Ellis, C., "The Chemistry of Petroleum Derivatives," Vol. II, New York, Reinhold Publishing Corp., 1937.
9. Heilbron, I., *et al.*, *J. Chem. Soc.*, **1934**, 1572–1575.
10. ——, ——, *Biochem. J.*, **29**, 1376–1381 (1935).
11. Herbig, W., "Die Öle u. Fette in der Textil-Industrie," Vol 3, Monograph Series Stuttgart, Wissenschaftliche Verlags, G.m.b.H., 1923.
12. Hilditch, T. P., "Industrial Chemistry of the Fats and Waxes," Covent Garden, WC2, London, Bailliere, Tindall, and Cox, 1927.
13. Holde, D., and Bleyberg, W., *Metallbörse*, **20**, 1855–1856 (1930).
14. Legg, V. H., and Wheeler, R. V., *J. Chem. Soc.*, **1929**, 2444–2499 (Modern plant cuticles); 2449–2458 (Fossil plant cuticles).
15. Lovern, J. A., *Dept. Sci. Ind. Research, Rept. Food Investigation Board*, **1934**, 89–92.
16. Machek, V., *Chem. Obzor*, **22**, 233–238 (1947).
17. Marcusson, J., *Z. angew. Chem.*, **37**, 413–414 (1924).
18. ——, and Lederer, P., *Chem. Umschau Gebiete Fette, Öle, Wachsen. Harze*, **38**, 253–255 (1931).
19. Maxfield, L. I., U. S. Patent 332,160 (1885).
20. Meyerheim, G., *Seifenfabr.*, **39**, 366–367, 394–396 (1919).
21. Molinari, E., "Treatise on General and Industrial Organic Chemistry," pp. 80–86, Philadelphia, P. Blakiston's Son & Co., 1913.
22. Nitsche, K. S., *Fette u. Seifen*, **46**, 391–397 (1939).
23. Ode, W. H., and Selvig, W. A., *Ind. & Eng. Chem.*, **42**, 131–135 (1950).
24. Pawleski, B., and Filemonowicz, C., *J. Chem. Soc.*, **56**, Abstracts (1889).
25. Porges, O., and Neumann, R., German Patent 180,637 (1905).

26. Potonié, H., *Ber. deut. pharm. Ges.*, **70**, 180–223 (1908).
27. Pschorr, R., and Pfaff, J. K., *Ber.*, **53B**, 2147–2162 (1920).
28. Pungs, W., and Jahrstorfer, M., German Patent 566,734 (1932).
29. Reilly, J., *et al.*, *Sci. Proc. Roy. Dublin Soc.*, **18**, 329–341 (1926); *ibid.*, 383–388 (1927); *ibid.*, **19**, 441–446 (1930).
30. ——, ——, *J. Soc. Chem. Ind.*, **56**, 231–238T (1937).
31. ——, ——, *Sci. Proc. Roy. Dublin Soc.*, **22**, 149–155, 181–185, 187–194 (1939).
32. ——, and Emlyn, J. A., *ibid.*, **22**, 267–272 (1940).
33. Romins'kii, I. R., *Mem. Inst. Chem. Technol. Acad. Sci. Ukr. S.S.R.*, No. 10, 133–160 [*Chem. Abstracts*, **33**, 5216 (1939)].
34. Roquette, R., *Química (Rio de Janeiro)*, **2**, 15–21 (1946).
35. Ryan, H., and Dillon, T., *Sci. Proc. Roy. Dublin Soc.*, **12**, 202–209 (1910); *Chem. Zentr.*, **2**, 2048 (1913).
36. Scheithauer, W., "Shale Oils and Tars," (Translated from the German by Stocke, H. B.), 2nd Ed., Revised, London, Scott, Greenwood & Son, 1923.
37. Sirahama, K., *J. Fac. Agr. Hokkaido Imp. Univ.*, **49**, Pt. 1, 1–93 (1942) (in English).
38. Smelkus, H., *Chem. Ztg.*, **48**, 409–410 (1924).
39. Stefanowski, W., and Dominik, Z., *Przeglad Chem.*, **1**, 73–76 (1937).
40. Stickdorn, K., U. S. Patent 2,285,100 (June, 1942).
41. Stremme, H., *Monatsh. Deutsch. geol. Ges.*, **1907**, 143–154.
42. Sundgrén, A., and Rauhala, V. Y., (Helsinki, Finland), *J. Am. Oil Chem. Soc.*, **29**, No. 12, 611–613 (1952).
43. Tisot, P. R., and Horne, J. W., "Waxes from Shale-oil Wax Distillate," *Bur. Mines Rept. of Investigations 4708* (July ,1950).
44. Tropsch, H., and Kreutzer, A., *Brennstoff-Chem.*, **3**, 49 (1922).
45. Von Boyen, E., British Patent 209,389 (1923).
46. Walter, Robt., *Ber.*, **59B**, 962–972 (1926).
47. Wartih, A. H., and Hanzely, E. M., Reports published in First Edition.
48. Zaloziecke, R., and Hausman, J., *Z. angew. Chem.*, **20**, 1141 (1907).
49. Zöllner, W., *Farben, Lacke, Anstrichstoffe*, **3**, 385–390 (1949).

5. Petroleum Waxes

Petroleum is the largest single source of the hydrocarbon waxes. Petroleum waxes are by-products of the petroleum industry in that the wax must be removed from the oil to produce lubricants with proper low-temperature characteristics. This gives petroleum waxes the advantage of a low price. The production of petroleum waxes in the United States has risen from 386,181,000 pounds in 1916 to 1,347,920,000 pounds in 1951. The largest single use of petroleum waxes thus far is in the manufacture of paper containers for packaging milk, the second largest in waxed wrappers for bread, and the third largest use in the manufacture of candles. These three uses required 57 per cent of the 908,000,000 pounds or thereabouts of petroleum waxes consumed in the United States.

Sources of Petroleum Waxes

Crude petroleums are essentially hydrocarbons since they usually contain more than 97 per cent of hydrocarbons, having a carbon content of 83 to 87 per cent, and a hydrogen content of 11 to 14 per cent; the remaining elements are oxygen, nitrogen, and sulfur.

The modern classification of petroleum hydrocarbons calls for the following groups: *paraffinic*, *aromatic*, *naphthenic*, *polyaromatic* (cyclic), *polynaphthenic*, and *asphaltic*, all of which more or less blend with one another. A petroleum may be fairly well balanced with respect to two groups, such as paraffinic and naphthenic; it is then referred to as paraffinic-naphthenic, e.g., Saurakhanui (so-called Surachany, Baku) crude.

The crudes not only differ from each other in the proportions they contain of the various hydrocarbon series, but in the degree of sulfur and other impurities. A "sweet crude," such as Appalachian, Oklahoma City, and East Texas, is free from an appreciable amount of impurities, whereas a West Texas, Ohio, or some California are of the "sour type" since they contain such impurities, and in considerable amount.

Pennsylvania (paraffinic) and Mid-Continent (paraffinic-naphthenic) crudes are good examples of paraffinic-base petroleums which on steam distillation will yield "cylinder stock" or wax-bearing raffinate. Of the Mid-Continent crudes Sachanen[41] states that Oklahoma City crude contains 36 per cent paraffin hydrocarbons, 45 per cent naphthenes, 14 per cent aromatics, and 9 per cent resins and asphaltines. Some of the Texan

crudes have a high wax content; e.g. East Texas, Longview 7 per cent, and Panhandle 6 per cent.

Of the foreign crudes Moreni (Roumanian) contains 4.8 per cent of wax, Iran crude contains 4.5 per cent of wax, Burma crude 8.0 per cent, and Assam 10.7 per cent[41]. Iraq, Kirkuk crude contains 1.9 per cent of wax. Venezuelan and Mexican crudes vary considerably in wax content; some are nearly wax free, such as Mexico, Tampico, while others carry as much as 3.5 per cent. Russian crudes, like the Gulf Coast crudes, have a naphthenic base; e.g., Russia, Baku carries little or no wax. However, the so-called waxy crude of Grozny (Russia) is rich in wax (6.5%).

Processes of Refining Petroleum

Four processes are in use in the refining of petroleum: (1) batch-type process; (2) continuous-type process; (3) pipe still process; and (4) vacuum still process. These processes will be briefly described.

Batch-type Process. In the refining of petroleum by the batch-type process a batch of crude oil of high API gravity (about 30 Bé) is run into what is known as a *crude coking still*. The process is termed "running to coke." In the operation of the still the fires are lighted and the distillation begun at about 200°F, when light gases such as propane and butane distil off. The heat is then increased to distil off a large fraction of light and heavy naphtha, a large part of which is reconstituted to make gasoline. The temperature is then raised from 400 to 475°F when kerosene distils over; a light fuel oil is distilled between 475 and 500°F. As the temperature is increased from 500 to 575°F cracking takes place and a gas oil distils off. When the fire is turned out and the still allowed to cool, there remains in the bottom of the still somewhat more than one-third of the original oil, which is pumped out and sold as fuel oil. However, a *wax-bearing raffinate* can be distilled off, after the gas oil, if a *batch shell still* is employed.

A modern batch shell still is a large cylindrical steel drum, perhaps 42 feet long, and 15 feet in diameter. A charge of 60,000 gallons or more of crude oil is run into the shell. The shell is horizontally mounted over a brick fire box; the heat is transmitted by flames to the bottom of the shell to the oil. The vapors, driven off from the oil by heat, pass into a vapor line which is part of the overhead equipment, and are led into a "heavy tower" where they are in part condensed, and then on to an "intermediate tower" where they are cooled and similarly condensed; the lighter vapors pass on also to be condensed by cooling. The liquid streams from the three cooling worms are thus produced from one still temperature, in contrast to the single steps of the older coking still process. The temperature of the still is then increased to recover additional streams of distillates by fractional condensation. These distillates are piped to temporary storage. After the naphthas and gas oil fractions (A) are distilled off, a fraction of 32 to 26°Baumé known as *paraffin distillate* (B) is taken off, followed by "paraffin slop" and "wax tailings" (C), leaving a residue of coke (D) in the still.

Continuous-type Process. Continuous crude stills are being used in refineries because of their greater productive capacity than the batch-type stills. The stills may be placed in series, hooked up in such a manner that each still is delivering a rectified cut, each with the fires trimmed to provide the heat required for the particular cuts on that still. The crude oil is pumped to one still (light naphtha end), flows through it,

is carried to the next still, and so on. The level of the oil in each still is held constant, and flue tubes can be used in the stills that require additional heat reinforcement. Wax distillates (B) are taken off at above 575°F, and the tar or fuel oil run off from the last still. The "slop oil" (C) which is a source of *microcrystalline waxes* has in the past been lost to the fuel oil taken off at the end. Operating on Mid-Continent crude the continuous-type process lends itself to the production of distillate for *paraffin wax* manufacture.

Pipe-Still Process. In more recent practice the distillation of Mid-Continent complete or "topped" crude is carried out in a pipe still, in which the heat is transferred through the walls of the tubes which pass directly through the furnace. The oil passes at a high velocity under pressure through the pipes or tubes and is discharged as vapor, without cracking, into a large fractionating column, i.e., a bubble tower equipped with bell caps, liquid seals, and overflow pipes. From the top of the column may be easily obtained an overhead distillate of petrol, and at the various "decks," or perforated plates at different distances from the top, may be withdrawn well-rectified fractions of higher and higher boiling point. The light ends are removed in the pipe still as described and subsequent cuts made in shell stills.

Vacuum-Still Process. The boiling point of a raffinate can be reduced by the use of a vacuum while distilling. Some refiners run the crude down to about 35° API in ordinary batch stills or continuous stills, and then transfer it to vacuum stills intended to take off the wax distillate. Bell[4] states that vacuum stills must be strongly braced to withstand external pressure. The wet vacuum system wherein the vacuum is maintained by pulling the condensate and fixed gas through a pump has been largely superseded by the dry vacuum system[4]. In the latter the vacuum is maintained by the removal of air and fixed gases by the vacuum pump. The condensates are trapped in receivers and periodically drawn off or are removed by another pump.

Wax Distillates

Wax distillates are obtainable with the batch-type, continuous-type, and pipe-still processes. They are not obtainable in the *cracking process*, because the hydrocarbons of the feed stock are chemically changed, or undergo pyrogenic decomposition, making recovery of paraffinic waxes well-nigh impossible. Naphthenic are preferred to paraffinic feed stocks for the best yields of petrol by the cracking process.

The wax-oil mixture that distils from petroleum below about 860°F contains wax that can be filtered from its oil in simple filter presses. In fractionating crude petroleum the "raffinate" or cut known as paraffin distillate, boiling from 170 to 310°C (338 to 590°F) when distilled at a very low pressure, can be separated into solid wax and liquid oil fractions by chilling and filter-pressing. The solid fraction that contains 65 per cent of wax is the *slack wax* which is sweated and refined to the regular paraffin wax of commerce (see Sweating of Slack Wax, p. 399). It is necessary to remove the wax from pressible wax distillate in order to improve the lubricating properties of the oil and make it chillproof. The wax distillate is therefore customarily pumped to the paraffin sheds, where it is allowed to repose in tanks to promote settling at the lowest room temperature. It is

then pumped through a bank of cooling units to hydraulic presses which squeeze out the wax from the chilled distillate (see Slack Wax, p. 395).

After the paraffin distillate is fractionated from the "crude" a higher boiling cut, known as the *high-viscosity fraction*, is distilled. This fraction also contains wax, but because of its microcrystalline nature does not lend itself well to separation and filter-pressing. The high-viscosity fraction is cold settled and centrifuged, thus yielding an oily wax portion, known as *petrolatum stock* and oil. *Petrolatum* can be refined from the petrolatum stock, or the *microcrystalline wax* in petrolatum stock can be separated by recrystallization and settlings from naphtha solution at reduced temperatures (see Microcrystalline Waxes, p. 421). This kind of wax is sometimes referred to as "petrolatum wax;" at least 85 per cent of its hydrocarbons are of a wax type, whereas petrolatum itself has only 25 per cent of hydrocarbons of a wax type.

Solvent Processes for the Rectification of Wax Distillates

Solvents play an important part in fractionating petroleum products. Rectification of distillates to free them from those aromatics which are undesirable (i.e., low V.I. (viscosity index) hydrocarbons, in order to obtain high V.I. lubricants) is accomplished by solvent extraction, employing solvent which will selectively extract the undesirable components so that a high-grade raffinate oil can be obtained. One of the earlier processes still in use is known as *Edeleanu*, and employs liquid *sulfur dioxide* for the purpose. Another in wide use today, for rectifying motor oils and the like, is that of *Stratford*, and employs *phenol* as a selective solvent. Pour point depressants are customarily added to such lubricants in their refined state. In all these systems the stratification takes place below the temperature of miscibility, allowing the two phases to be separated either in "settlers" or in a "countercurrent contacting tower," or by centrifuge as in the separation of the *microcrystalline waxes* from the slop oil of low V.I. value.

A chlorinated solvent known as "*Chlorex*," and also *nitrobenzene* find extensive use; these solvents have low miscibility temperatures with the feed stock, allowing the separation, which is naturally lower than the miscibility temperature, to be made at low temperatures. A process known as the *Duo-Sol process* employs a double step of extraction, in which *cresylic acid* frees the low V.I. aromatics and the deasphalting itself is done by means of *propane*, very efficient in rejecting asphalt. The process utilizes the countercurrent principle.

Furfural has come into use as an important selective solvent for single extraction of high-viscosity lube oils. Furfural is an aldehyde obtained by the distillation of corn husks or grain refuse with sulfuric acid; it is relatively inexpensive, and used in a similar manner to phenol in solvent ex-

traction procedure. Microcrystalline waxes are important by-products which are recovered from the furfural extractant (see p. 383).

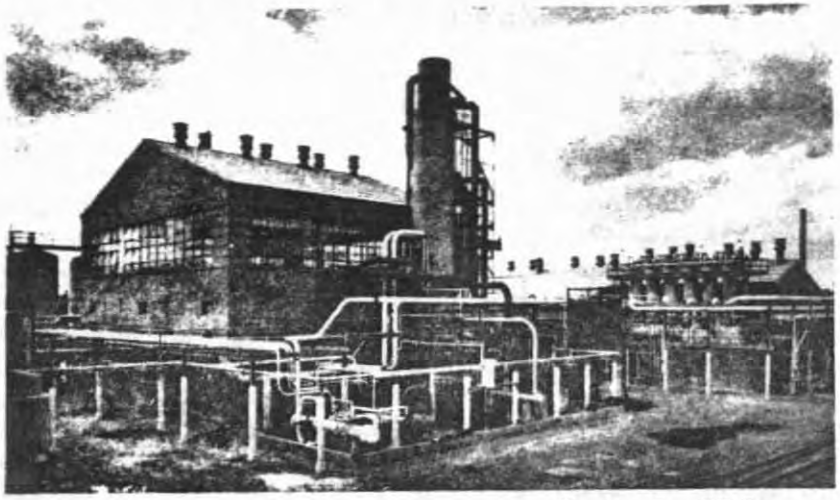
Solvent Dewaxing Plants

In the customary preparation of base oil stocks there are five distinct phases in the modern refining process: (1) vacuum distillation of the topped crude; (2) propane deasphalting to obtain the raw lube stocks; (3) furfural refining of the latter to obtain a waxy raffinate; (4) methyl ethyl ketone (MEK)-benzol dewaxing of latter to obtain wax; (5) clay finishing of dewaxed raffinate to obtain finished oil stocks.

The first solvent dewaxing plant that employed acetone-benzene azeotropic mixture was constructed in 1927. This principle of dewaxing replaced frame and filter presses and centrifuge processes which were subject to sharp limitations of being restricted to crystalline and amorphous stocks respectively. Propane solvent type dewaxing plants were subsequently developed and MEK replaced acetone, resulting in lower pour point oils for the automobile industry.

The Cities Service Company operates one of the largest petroleum wax refineries in the world at Lake Charles, Louisiana. The output is somewhat over 87,200,000 pounds of fully refined wax per annum. It was erected at an original cost of about $45,000,000. It has two separate units for the dewaxing of all solvent refined raffinate stocks by the MEK solvent dewaxing process.

Waxy lube oil from the refinery's solvent unit is diluted with special solvents upon receipt at the MEK unit. This solvent is principally methyl ethyl ketone. Mixed with waxy oil, it is piped into chilling exchangers and the temperature is reduced to well below 0°F by propane refrigeration. At this temperature, the solid wax crystallizes from the oil-solvent mixture. The mixture of solvent, oil, and wax is then piped onto cylindrical, canvas-covered rotary filters 20 feet long and 10 feet in diameter. The wax cake built upon the surface of the rotary filter is removed by scrapers and is redissolved in hot solvent. The mixture of warm solvent and wax is then chilled by propane refrigeration to 50°F, to remove more of the softer waxes with higher oil content. During the recrystallization treatment in the rotary filters, partially refined wax builds on the surface of the filters while a mixture of soft, low melting point wax and solvent is continuously drawn off from the center. The mixture of solvent and soft wax is sent through a solvent recovery system which returns solvent to the unit and sends soft wax to the storage tanks. The wax cake on the surface of the filter is carefully washed with cold solvent to remove any traces of oil or soft wax. The partially refined wax is stripped from the surface of the rotary filter and the solvent removed by steam stripping; the wax is next



Courtesy Sun Oil Company

FIGURE 11. Modern solvent dewaxing plant.

sent through a dehydrater to remove all traces of moisture. It is then pumped into a percolation type filter with bauxite which removes all traces of color, odor, and taste. After slow passage through the filter, the fully refined wax is piped to tank cars or to the slabbing machines.

The Sun Oil Company at Philadelphia, Pennsylvania operates a solvent dewaxing plant (Figure 11) in which the wax is removed from lube oil stocks. The lube oil and solvent are chilled (Figure 12) and the wax crystallized and removed on a "rotary piltex" such as pictured in Figure 13. These operations apply to the recovery of both paraffin and microcrystalline waxes.

In the selective solvent process in operation by the Union Oil Company, at Oleum, California, the waxy oil is heated to above the pour point and is then pumped through double pipe scraped heat exchangers where it is cooled to a predetermined temperature at which the desired wax will have crystallized from solution. The thick paste of wax crystals is further refined with the aid of a suitable solvent to de-oil the filter cake. (See details of process as described under "Aristowaxes," p. 416.)

The Bayonne Refinery of the Esso Standard Oil Corporation operates a new dewaxing plant which employs solvent extraction. The selective solvent is methyl ethyl ketone (MEK). The feed stock is chilled with a mixture of MEK, benzene, and toluene. The wax produced is known as *slack wax* and contains up to 10 per cent oil. The process is automatic.

Paraffin distillate or feed stock is mixed with the solvent and heated to about 125°F. More solvent is added and the mixture refrigerated for wax

crystallization. It is then fed to a rotary-type vacuum filter with a cloth-covered cylinder 10 feet in diameter and 16 feet long, the mixture temperature being 17 to 20°F. Each revolution of the drum requires 1.5 minutes and as it revolves, the lower portion passes through the solvent-wax-oil mixture. A vacuum inside the drum draws the solvent-oil through the cloth, causing a wax-oil concentrate to deposit on the surface. As a means of further reducing the oil content, fresh solid, oil-lean solvent is allowed to flow over the up-coming wax cake on the filter drum. Compartments within the drum collect the solvent for recycling.

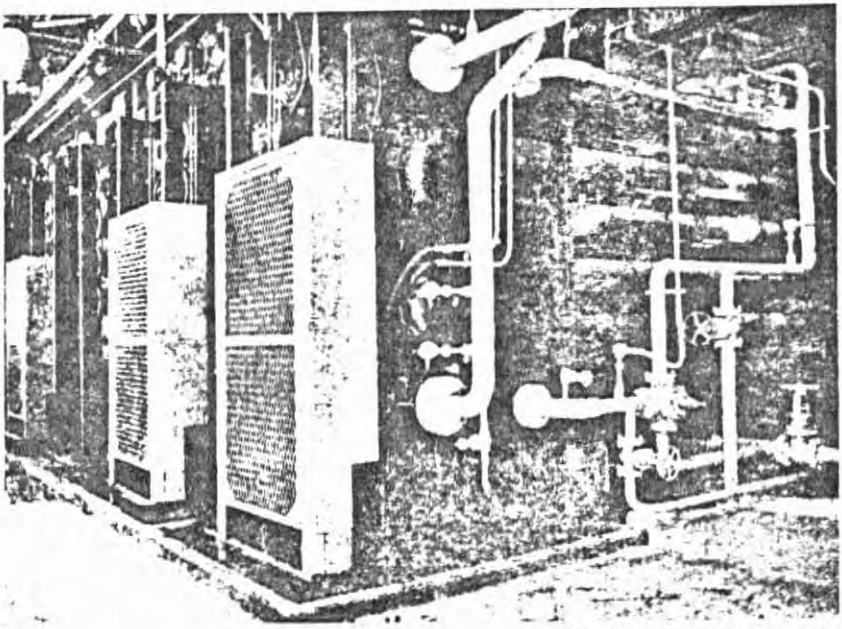
Manley Process of Dewaxing Wax-bearing Oils

In the Manley[27] process the wax-bearing oil is mixed with about twice its volume of a diluent comprising *propane* and *butane*, and the dilute mixture is chilled while flowing in a confined stream in indirect heat-exchange relation with a cold portion of the diluent undergoing refrigerative evaporation. The dilute stream is chilled to a temperature of −18°C or below to solidify the wax. The solidified wax is separated from the cold mixture, and the diluent contained in the dewaxed mixture is subjected to refrigerative evaporation in indirect heat-exchange relation with the aforesaid confined stream of dilute mixture to effect its cooling. According to Manley, the cold dilute mixture while under super-atmospheric pressure is subjected to filter-pressing, forming a filter cake of solid wax. A stream of dewaxed filtrate is continuously removed from the filter and sufficient pressure is imposed on the filtrate stream to prevent substantial vaporization of the diluent from the oil during filtration. Microcrystalline waxes of both softer and harder penetration are thus recovered.

Furfural Refining Process

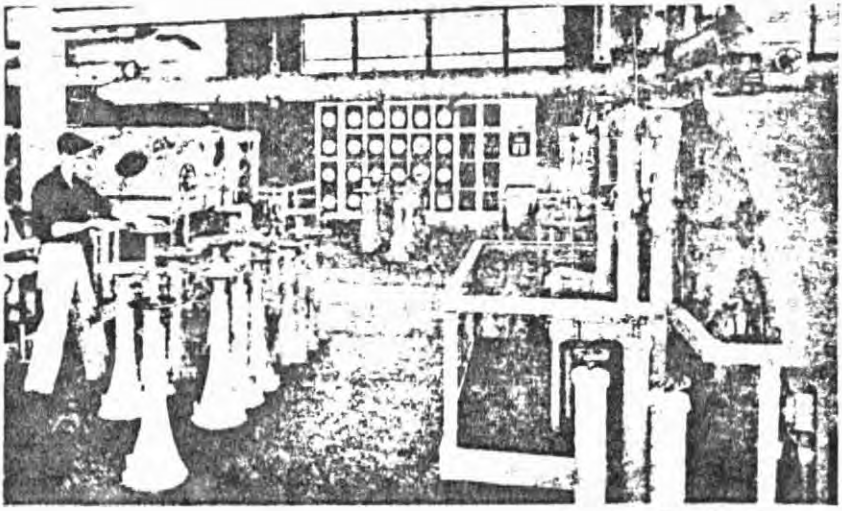
When a raw lubricating fraction is mixed with furfural at 95°C, it is possible to form two liquid phases, one a lighter phase which can be separated as a raffinate that contains roughly 90 per cent of refined oil and 10 per cent of furfural. The heavier phase from the raw lube fraction, which has been separated from the refined oil raffinate, consists of furfural (90%) and the wax-resin-pitch impurities (10%)[26]. The furfural is distilled off, and the crude wax-resin-pitch is sold to manufacturers of molded rubber goods.

After the removal of the furfural from the oil raffinate it must be dewaxed. This is accomplished by mixing it with a mixture of methyl ethyl ketone and benzene, at a temperature of about 120°F. The solution is passed through double-pipe heat exchangers where some refrigeration is recovered from the cold filtrate solution from the rotary vacuum filter[3]. The solution is further chilled (to about 35°F) by direct expansion of ammonia to double-pipe chillers which are equipped with scrapers to prevent



Courtesy Sun Oil Company

FIGURE 12. Double pipe exchangers used as chillers in a solvent dewaxing plant.



Courtesy Sun Oil Company

FIGURE 13. Enclosed rotary filters for solvent deoiling process.

the accumulation of solid wax on the inner surface of the center pipes. The chilled solution with wax slurry flows from the double-pipe chiller to the rotary vacuum filter.

The drum of the filter rotates and the level of the solvent-oil-wax mixture is such that about one-half of the drum is submerged. A cake of wax forms on the drum and as the waxy layer approaches the top in its rotation it is sprayed with chilled solvent. A vacuum inside of the drum causes filtration on the submerged portion of the drum and the cake of wax may be dried by an inert gas (such as CO, CO_2, N mixture) which can be pulled through the cake because of the resultant positive gas pressure. When the wax cake approaches a scraper blade it is allowed to fall into a screw conveyor which discharges the slack wax to a surge tank. From this tank the wax is pumped to the wax flash tower where the major part of the solvent is distilled off. Removal of the last traces of solvent is done by steam stripping in the wax stripping tower. The stripped wax is cooled and pumped to storage.

The liquid wax from storage tanks, adjusted in temperature to a few degrees above its solidification point, is (a) ejected from a hopper by a piston into pans which are then cooled by refrigerated air as they travel on a continuous chain conveyor; or (b) is rammed intermittently through a slot which is of the width and thickness of the wax slab. The extruded ribbon is immediately chilled by passing it through cold water. The continuous thick heavy band is picked up by a large rotary wheel and conveyed to a flying shears to cut it into the required slab lengths suitable for packaging.

Separating Wax Crystals by Solvent-Aides

According to Dons and Mauro[11] the separation of the wax from the oil can be effectively accomplished by (1) precipitating the wax in a cooled dewaxing solution; (2) extracting the main body of relatively free oil solution from the coalesced wax crystals; and (3) subjecting the wax to forcible disintegration and deoiling operations so that previously trapped solution is removed with the wax. The system proposed brings about simple cleaning action. A stream of wax clusters and oil solution is discharged into a settling zone, where the clusters readily separate and then pass into a disintegrating zone associated with a deoiling zone where each minute wax particle is forcibly cleansed by a counter-flowing solvent stream.

The solvent selected should be an excellent oil solvent, but poor wax solvent and one which will retain a low viscosity even when containing much oil in solution. Good solvents for the purpose appear to be the ketones, e.g., methyl ethyl ketone. Other solvents include methyl chloride. methyl acetate, and chloroethane. Blends may be selected which avoid fire hazard, such as carbon tetrachloride (50), acetone (50); or perchloroethyl-

ene (50), isopropyl acetate (40), and dichloroethyl ether (10). For convenience in commercial practice a simple combination of methylene dichloride and dichloroethyl ether ("Chlorex") has been found very effective.

Filtration Refining of Lube Oils and Wax Stocks

The process of removing color and deleterious compounds from lube oils is termed "filtering," although the actual decolorization of oil is really a process of adsorption. The process is selective and it so happens that the very color-forming resinous and asphaltic bodies that are undesirable are the ones that are most susceptible to this adsorption phenomena. The adsorbents in use in the oil industry are fuller's earth, bone char, special clays, alumino-gel, and prepared vegetable chars. Clays originate in Florida, Georgia, Texas and in California and other western states. Filter clays must be kiln-fired before use, and are recovered for reuse by burning them in clay burners. An exception is an acid-treated one time clay. The choice of clay and the size of the clay particle depends on individual preference; a 30–60 or 40–60 mesh clay is generally preferred.

If the clay treatment of the microcrystalline wax is done with naphtha-diluted stock the procedure is called *solution percolation* or solution filtration. If percolation is done with an undiluted stock it is termed *straight percolation*, or straight filtration. A filter used in percolation is a steel cylinder with a perforated plate and canvas blanket at bottom which holds the clay, but allows the oil to percolate through it. Pressure is applied to increase the flow. Naphtha must be removed from the clay bed by blowing steam through for a considerable length of time, before the filter can be dumped. For straight percolations steam-jacketed filters must be used.

For subsequent bleaching with activated clays, see p. 389.

Crystalline Types of Petroleum Waxes

It was observed many years ago in the sweating of the solid paraffin waxes at the petroleum refinery that three crystalline manifestations of hydrocarbons are encountered. These are known as "plate," "malcrystal," and "needle." It was also recognized that the relative proportion of these types of crystals bears a relation not only to the source of the crude, but to the method of handling the wax in the sweating and filter-press operations.

Present refining methods, particularly sweating, have a tendency to remove the ill-defined or malcrystals and the "large needles" which are common to the lower hydrocarbons, so that the finished waxes for the most part approach the plate type in which the crystals are hexagonal plates. The microcrystalline waxes now recovered from the still residuum are of the plate type, but the crystals are of extremely small or microscopic in size.

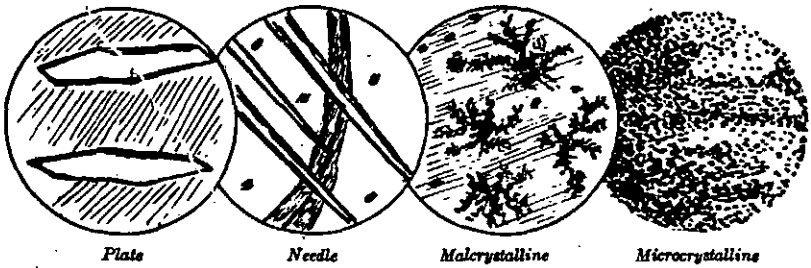


FIGURE 14. Types of wax crystals obtained from dilute solutions of the wax in nonpetroleum solvents.

Padgett, Hefley, and Henriksen[34] found that the crystals from residual oils, petrolatum, and heavy raw-wax distillates were small even after substantial removal of the bitumen and repeated precipitations from acetone, and were much smaller than the smallest crystals found in slack wax. It is generally believed that the microcrystalline characteristic is associated with hydrocarbons with side chains, but that such wax when distilled will yield normal macrocrystalline hydrocarbons on cracking. (Also see Crystal Habit of Paraffin Waxes, p. 405.)

Wax Hydrocarbons of Petroleum Waxes

Marcusson[28] in 1915 attempted to show that the protoparaffins left in undistilled petroleum wax are branched-chain hydrocarbons by converting the paraffins to aliphatic acids with oxygen in the presence of manganese dioxide and fuller's earth. He treated 20 grams of petroleum ceresin (m. 62–71°C) with oxygen in the presence of manganese dioxide deposited on fuller's earth, at 125°C for 35 hours, then for 55 hours at 150°C. The resultant soft material was separated into saponifiable and unsaponifiable parts by the method of Höning and Spitz, giving 44 per cent of unsaponifiable. The latter portion had an iodine number of 8.5, and acetyl value of 21.0. The acids were separated by Varrentrap's method, giving oily acids and solid acids. The oily acids contained no hydroxy acids and had an iodine number of 11, acid value of 115, and density of less than 1; they were considered polymerized unsaturated acids. The solid acids had a melting point of 60 to 62°C, a molecular weight of 384, and an acid number of 146; they were extremely soluble in ordinary organic solvents, which is typical of branched-chain acids. Marcusson concluded that branched-chain hydrocarbons are present in ceresin or protoparaffin as a major constituent.

Hydrocarbons of as high a molecular weight as that of $C_{70}H_{142}$, heptacontane (m. 105.5°C), have been properly identified; those of still higher molecular weight have been synthesized.

Although a crude such as Appalachian may be made up almost entirely

of normal straight-chain hydrocarbons, upon distillation these hydrocarbons change appreciably to isomeric paraffinic, olefinic, and naphthenic—the latter being like olefinic but in closed chain formation. The solid or waxy portions, according to Mabery[25], tend to retain the C_nH_{2n+2} structure.

Buchler and Graves[5] in 1927 examined the hydrocarbons of various petroleum waxes, and reported as to the range of carbons and many of their physical constants.

Paraffin wax is listed as having 14 hydrocarbons ranging from $C_{18}H_{38}$ to $C_{32}H_{66}$, solidifying between 27.0 and 68.9°C (80.5 and 156.0°F). *Petrolatum wax*, which is a microcrystalline wax, has hydrocarbons ranging from $C_{34}H_{70}$ to $C_{43}H_{88}$ inclusive. Its solidifying range is 71.0–83.8°C (159.7–182.7°F); refractive index ($n_D^{84°}$) 1.4323–1.4378; density ($d^{84°}$) 0.7706–0.7803; molecular weight 474–603.

Slop wax has 13 hydrocarbons ranging from C_{26} to C_{43}, solidifying between 55.7 and 83.3°C (132.2 and 182.0°F). *Rod wax* has 8 hydrocarbons ranging from C_{35} to C_{41}, solidifying at 73.9 to 82.5°C (165.0–180.5°F).

The petroleum waxes were all taken from a Salt Creek, Wyoming crude. The paraffin wax was obtained by pressing the wax distillate at −17.8°C (0°F), the slop wax from the heavy distillate in the coking process; the petrolatum wax was centrifuged from residual stocks at −17.8°C (0°F); and the rod wax collected from the sucker rods in the field.

Each wax was recrystallized from ethylene dichloride at 4°C (24°F) until a wax of constant melting point and index of refraction was formed. Such fractions were then used as a basis for determining the composition, and for establishing the fact that the series is a homologous one of saturated hydrocarbons irrespective of whether the wax is crystalline or in an amorphoid state.

The petroleum waxes have a specific heat value of 0.6. The latent heat of fusion is 35 to 39 calories per gram. The dielectric constant (s.i.c.) is about 2.4 at 30°C and declines to 2.1 at 85°C. The dielectric strength (K.V.) is 50 plus at 30°C; 31 to 38 at 70°C, and 35 to 41 at 100°C. The optimum vapor pressure at 120°C is 0.001 (mm Hg).

Melting Points and Specific Gravities of Wax Hydrocarbons

The values given below show the relation between the molecular weight, expressed as the number of carbon atoms, and the melting points and specific gravities for (a) normal paraffin hydrocarbons, and (b) petroleum ozokerite hydrocarbons. The latter contain a large proportion of branched-chain paraffins, to which are attributed the oil adsorptive characteristic of ozokerite. The values are based upon the data of Sakhanov[42].

Number of Carbons	Melting Point (°C)		Specific Gravity (d^{100})	
	(a)	(b)	(a)	(b)
C_{20}	37	—	0.734	—
C_{25}	54	29	0.748	0.777
C_{30}	66	39	0.759	0.779
C_{35}	74	50	0.767	0.782
C_{40}	81	60	0.773	0.784
C_{42}	85	67	0.781_{90}	0.785
C_{50}	92	81	—	0.786
C_{54}	95	90	—	0.787

Viscosity (in Poises) of *n*-Hydrocarbons

The values given below are for liquid hydrocarbons near their freezing points, by Gillet and Drickamer[17]; paraffin wax hydrocarbons C_{21} to C_{36}, by Mazee[29]; and miscellaneous C_{36} to C_{53} *n*-hydrocarbons associated with ceresins.

Liquid		Paraffin		Ceresin	
C_5	0.00232	C_{21}	0.0181	C_{37}	0.0700
C_6	0.00310	C_{22}	0.0220	C_{40}	0.0790
C_7	0.00410	C_{24}	0.0242	C_{42}	0.0872
C_8	0.00539	C_{29}	0.0340	C_{50}	0.0940
C_{10}	0.00907	C_{30}	0.0404	C_{53}	0.1000
C_{12}	0.0149	C_{31}	0.0437		
C_{14}	0.0229	C_{34}	0.0514		
		C_{35}	0.0557		
		C_{36}	0.0589		

Melting Points vs. Molecular Weight

Number of Carbons	Molecular Weight	Melting Points (°C)	
		n-Long-chain Hydrocarbons	Branched-chain Hydrocarbons (av.)
C_{20}	282.54	37 (98.6°F)	
C_{25}	352.67	54 (129.2°F)	29 (84.2°F)
C_{30}	422.80	66 (150.8°F)	39 (102.2°F)
C_{35}	492.93	74 (165.2°F)	50 (122.0°F)
C_{40}	562.06	81 (177.8°F)	60 (140.0°F)
C_{44}	619.16	88 (190.4°F)	68 (154.4°F)
C_{50}	703.32	92 (197.6°F)	81 (177.8°F)
C_{54}	759.42	95 (203.0°F)	90 (194.0°F)

Bleaching of Petroleum Waxes

Bleaching of Hydrocarbons by Clay. Fuller's earth is a form of clay which is a natural, earthy, fine-grained material with a high capacity for decolorizing oils. It is composed of minerals that are hydrous magnesium aluminosilicates in their chemical composition. The name "fuller's earth" is derived from its first use, which was the removal of grease from woolen

cloth in the process of "fulling" or "shrinking." Some clays are naturally active, such as fuller's earth; others are naturally inactive and develop their oil decolorizing ability only by treatment with acid. Bentonite is an example of the latter type; it is formed by the natural wetting of volcanic ash.

There are two processes used in decolorizing oils by clays, namely, the percolation process and the contact process. For the percolation process only fuller's earth is used; it is in granular (30–60 mesh) form. The percolation tanks are 5 to 10 feet in diameter and from 20 to 30 feet high. After use clay must be cleaned with solvent; residual solvent is blown out by steam, and the clay is removed and fired at a high temperature to revivify it. In the contact process fine and coarse earth are mixed with the oil in a large vat, heat is applied, and after mixing the batch is placed in a filter press and the oil squeezed from the clay. Acid-activated bentonites are used for the contact process.

The depth of clay for oil filtration should be about 15 feet but for wax a depth of 5 or 6 feet is sufficient. Increasing the depth provides greater clay charging capacity, and results in increased lengths of runs. A yield of 20 to 30 barrels of wax can be obtained per ton of clay.

The decolorizing efficiency of fuller's earth is greatly enhanced by the Hartshorne process. After the clay is mined, it is permitted to dry for a few days, and then crushed to coarse lumps. Thereafter it is dried in a rotary kiln to reduce the moisture to about 20 per cent, ground by grinding rolls, and screened to the various sizes. Hartshorne introduced three additional steps, namely (a) further grinding of the crushed lumps; (b) mixing of water with ground earth as in a pug mill; and (c) subjecting the earth to flow under high pressure, as in an extrusion apparatus. Subsequently the extruded earth is dried, ground, and sifted to the desired size. The extruding pressure at the extrusion die is about 500 pounds per square inch, and this disrupts the particles of the earth in such a manner as to greatly increase its decolorizing power.

An active bleaching clay known commercially as "Tonsil"[47] originates from argillaceous strata located on both sides of the middle and lower course of the River Isar in Bavaria, Germany. It, like English fuller's earth, is a hydrated magnesium aluminum silicate, the individual particles being of a colloidal nature. The average composition shows a high content of silica: SiO_2, 72.5 per cent; Al_2O_3, 13 per cent; Fe_2O_3, 5 per cent; MgO, 1.5 per cent; CaO, 0.8 per cent; loss on ignition, 7.2 per cent. As processed from the HCl acid washed raw clay, the resultant dry bleaching clay takes up the coloring matter from waxes by a process termed "adsorption."

Rod Wax—A Natural Crude Oil Wax

Rod wax is formed by spontaneous precipitation from crude oils in sucker rods or in storage; it contains high molecular weight hydrocarbon waxes of

the ceresin type. A wax of the same type is deposited on the walls of tubes used for pumping paraffinic crudes[25].

The composition of rod wax has been of great interest since it represents wax which is natural to petroleum that has not undergone the pyrogenic changes to which petroleum is subjected in its refining. The content of petroleum wax in raw rod wax varies from 50 to 70 per cent, the remainder being oils and asphaltic resinous substances[33].

Hydrocarbons of as high a molecular weight as that of $C_{70}H_{142}$, *heptacontane* (m. 105.5°C, or 222°F), have been properly identified. Mabery[25] examined the paraffine of a rod wax, settled out of Pennsylvania crude and collected in the well pumping equipment. He found hydrocarbons extending beyond $C_{35}H_{72}$ (m. 76–77°C, or 169–171°F). Reistle and Blade[39] gave the melting point of purified rod waxes as from 55–82°C (130–180°F). Buchler and Graves[5] found C_{35}–C_{40} hydrocarbons in a Wyoming crude oil wax from sucker rods. Nenitzescu and Irimescu[32] obtained fractions from Romanian *crude* rod wax: (a) a fraction having *37, 38, 40, 41, 42,* and *44 C* atoms, and (b) another fraction containing principally *43, 46, 49,* and *52 C* atoms with smaller amounts of paraffins having *41, 42, 44, 45,* and *47 C* atoms. By means of selective solvents consisting of ethanol, ethanol and benzene in varying proportions, and propanol, these investigators obtained different groups of paraffins from rod wax, and a residue with average molecular weights from 486 to approximately 1200, indicating paraffins having *35* to *80 C* atoms per molecule.

"Waxed In" Oil Wells. Wax accumulates in the oil well casing, and impedes or interrupts the flow. A chemical is added which affects softening, and has a dispersing solvent action on the wax.

Classification of Refined Petroleum Waxes

It is difficult to draw up a classification of petroleum waxes that could not be subject to criticism. The classification here given is somewhat different from others that have been proposed; it comprises the various types of waxes produced in American refineries.

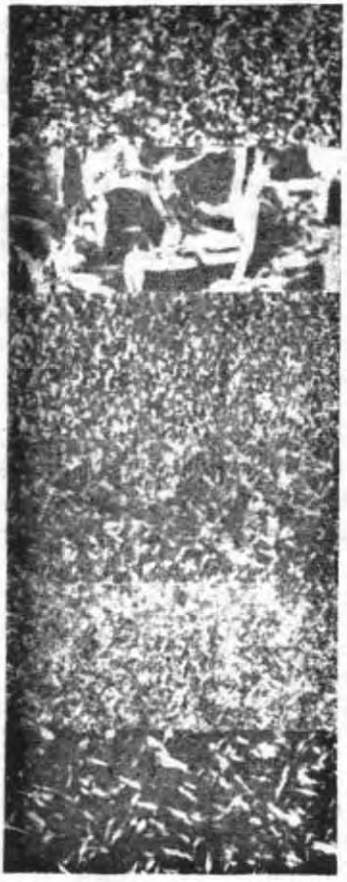
(1) Paraffin Wax Group
  (a) Softer paraffin waxes (e.g., slack waxes)
  (b) Intermediate paraffin waxes (e.g., scale waxes)
  (c) Harder paraffins (e.g., fully refined waxes)
(2) Petrolatums
(3) Microcrystalline Wax Group
  (a) Medium soft (e.g., "Petrowax")
  (b) Medium hard (e.g., "Petrosene A")
  (c) Hard (e.g., "Be Square 190/195")

These three groups can be distinguished by their crystalline character-

istics. Group (1) waxes have relatively large crystals (macro crystals). The slack or subscale waxes contain more oil than scale waxes, and the melting points usually are between 122 and 140°F. The scale waxes have negligible tensile strength and the melting points are between 118 and 135°F. The fully refined waxes (block paraffines) range in melting point from about 123 to 165°F, but usually from 126 to 146°F.

Group (2) which are not true waxes have crystals so minute because of occluded oil that they can be regarded as amorphoid (amorphous-like) in structure. Not much more than 25 per cent of the hydrocarbons of petrolatum are waxlike.

Group (3) waxes have very minute crystals (micro crystals) and are of high melting point, generally above 145°F and exceptionally as high as 200°F. Waxes which are by-products of the *motor oil raffinate* have 26 to 42



—Microcystalline wax, m. 160°F

—Paraffin wax, m. 130°F

—Microcrystalline wax, m. 180°F

—Ozocerite, m. 160°F

—Carnauba wax

—Beeswax

Courtesy Barco Oil Co

FIGURE 15. Crystal habit of waxes. Magnification 150×.

carbons, melt within the range of 145–175°F, and have an SUS viscosity at 210°F of about 55 seconds. They have needle-like crystals, and are somewhat brittle. These waxes are sometimes referred to as "micro waxes." Waxes which are prepared from *distillation residuals* have 36 to 70 carbons, melt within the range of 145–175°F, and have an SUS viscosity at 210°F of about 55 seconds. They have small needle-like crystals, and are flexible. These waxes are sometimes termed "petrolatum waxes." Waxes which have been recovered from *tank bottoms* of crude oil have 40 to 75 carbons, melt within the range of 180–200°F, and are hard. They have very small needle-like crystals.

The medium soft microcrystalline waxes have a needle penetration of 25 to 80 (100 g/77°F/5 sec); the medium hard waxes have a value of 10 to 25; and the hard waxes a value of 3 to 10. Penetrations are determined by the ASTM D5–25 method; the values are expressed as mm actual penetration × 10.

Roughly speaking, *paraffin waxes* come from the dewaxing of paraffin distillates, *petrolatum* from high-viscosity lube distillates, and *microcrystalline waxes* from residuum. In dewaxing the paraffin distillates, the various steps along the way, to almost complete freedom from oil, yield *slack wax*, *scale wax*, *semirefined wax*, and finally *fully refined paraffine*.

PARAFFIN WAXES

Specific Sources of Paraffin Waxes

Paraffin wax occurs associated with paraffinic-base oils in many crudes. The wax content of the *wax-bearing raffinate* from the crude is about 10 per cent. A pressible Pennsylvania distillate has a gravity of about 34 API, and a viscosity of 70 seconds Saybolt at 100°F or even higher viscosity. To obtain a chillproof high-grade lube oil it is necessary either to recover the wax from the raffinate or to treat it with a pour-point depressant.

Mid-Continent (Arkansas, Louisiana, and Oklahoma) oils provide a better economic source for a paraffin wax by-product than do the Appalachian (Pennsylvania and West Virginia), and are thus extensively employed. A pressible wax distillate of Mid-Continent origin has a gravity of 30 to 31° API. California oils, on the other hand, carry little or no wax, e.g., Midway is almost wax free. Gulf Coast crudes, however, vary from naphthenic oils with almost no wax to oils such as Rodessa which contain more wax (5.2 %) than the Appalachian (2.4 %). Differences in the physical characteristics of the paraffin waxes can often be ascribed to the origin of the crude, and the particular refinery at which such a crude is handled.

Recovery of Paraffin Wax Group

There are ordinarily three principal types of wax encountered in crude oil, namely *paraffin wax*, *slop wax*, and *petrolatum*. The first is contained in

distillates from which it may be pressed. When Pennsylvania crude, or other paraffin wax-yielding petroleum is distilled by the *batch-type process* (see p. 378), using a cylindrical still, there are five steps to this method of distillation. The first out yields light naphtha, the second heavy naphtha, the third high test burning oil, and the fourth low test burning oil; the fifth portion is the undistilled residuum, which is the source of paraffin wax. This residuum is pumped to the *tar still*, which holds about 200 barrels, and is reheated with high-pressure live steam to the point at which it will again give off the desired vapors. A *heavy distillate* is taken off which is wax bearing and pressible. About 5 per cent of tar coke remains in the still and is recovered for sale to the industries.

Paraffin wax is also recovered by the *continuous-type process* which has already been described (see p. 378). A *continuous tower still* (pipe still with fractionating column, referred to on p. 379) is a less expensive process since it yields a wider range of products in the same run, and has a much lower cost of maintenance. With a tower still it is not necessary to pump the residuum to a separate tar still. The *heavy distillate* is taken off at the first trap; it is *wax-bearing*, and in the last part of the run is known as *wax tailings*. An "intermediate distillate" or raffinate is taken off at the second trap, and a "light distillate," which is a raffinate of high test oil, such as 300 oil, is taken at the third trap.

The heavy distillate above referred to is one which distils over at 315 to 425°C (600–800°F), and contains not less than 6 to 8 per cent of wax. This *wax-bearing distillate* goes to the "chill rooms," where cooling to a temperature of 25 to 30°F is effected by pumping the distillate through tubes jacketed by cold brine and provided with helical scrapers. The resultant crystal mush is subjected to powerful pressure by plate and frame filter presses set in refrigerator rooms, and the heavy oil raffinate which drains off from the press is collected as lubricating oil. It is known as "spindle oil" and has a gravity of 32° Baumé and a pour point of plus 6 to 7°C (20°F).

The press cake ("slack wax") which may contain as much as 50 per cent or more of wax may be broken up, melted, chilled, and sweated to form *scale wax*, which contains 1 to 6 per cent of oil, and *foots oil*, made up of lower melting point wax plus oil (see Sweating of Slack Wax, p. 399). The scale wax is then refined to paraffin waxes of different melting points, leaving a *slop oil* which is of little or no value (see Production of Paraffin Wax at the Refinery, p. 399).

Paraffin waxes consist of mixtures of purely paraffinic compounds, whereas the dewaxed stocks (e.g., slop oil) from the heavy distillate consist essentially of compounds containing up to eight aromatic or naphthenic rings with paraffin side chains.

Softer Paraffin Waxes

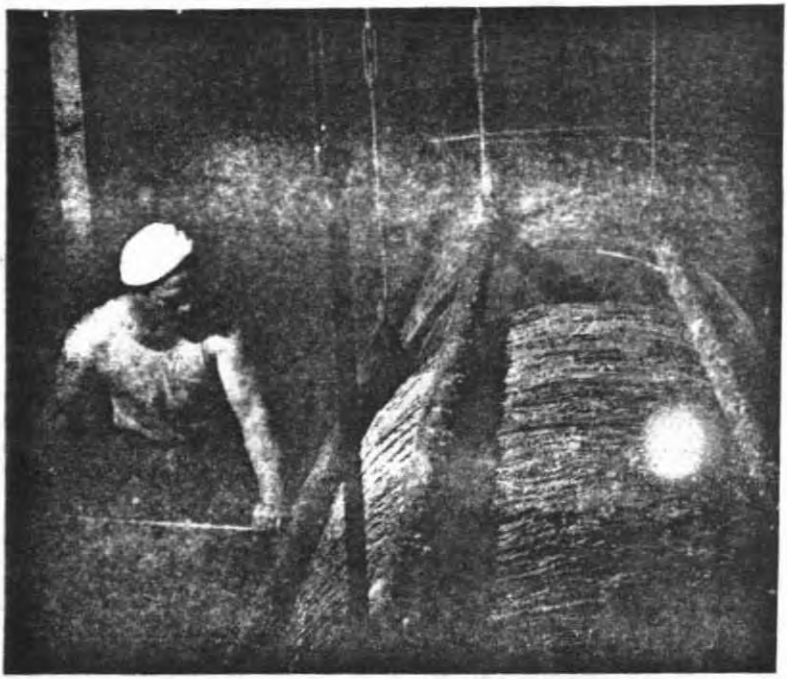
The softer paraffin waxes include *slack wax* and *sweat wax*, the latter a more oily by-product of the former. In the refinery the crude oil raffinate known as "paraffin distillate" (wax distillate) has a boiling point range of 170–310°F when distilled at a very low pressure. To separate the paraffin wax from the oil, the wax distillate may be chilled until the wax crystallizes, and the resultant slurry may be filter pressed. If the wax forms a filter cake from which the oil drains easily the wax distillate is said to be "pressible." If the oil cannot be separated well from the wax crystals in the pressing operation, the wax distillate is "unpressible." The wax left on the filter presses is called *slack wax*. The consistency of slack wax may be soft or semisolid and the oil content is normally 10 to 35 per cent.

Slack Wax. The paraffin distillate at a temperature of 80 to 100°F is pumped to the *paraffin sheds* (wax plant), where it is allowed to repose in tanks to promote settling at the lowest room temperature (between 0 and 32°F). It is then pumped through a bank of cooling units (*wax chillers*) to *hydraulic presses* which squeeze out the wax from the chilled distillate. The cooling units, usually "double-pipe horizontal" or "double-pipe vertical" chillers, consist of a series of pipe coils placed in a steel jacket of circulating liquid ammonia. One section of a double-pipe chiller will reduce the temperature of 30 barrels of distillate from 90 to 15°F in twenty-four hours.

Some wax plants use a vertical double-shell tank chiller, known as the "Gray unit;" the distillate enters at the top of the inner shell and leaves at the bottom. The refrigerant enters at the bottom of the outer shell, passes around the inner shell, and leaves at the top. Through the inner shell extends a shaft filled with arms carrying scrapers; these are thrown against the inner surface as the shaft revolves driven by an overhead mechanism.

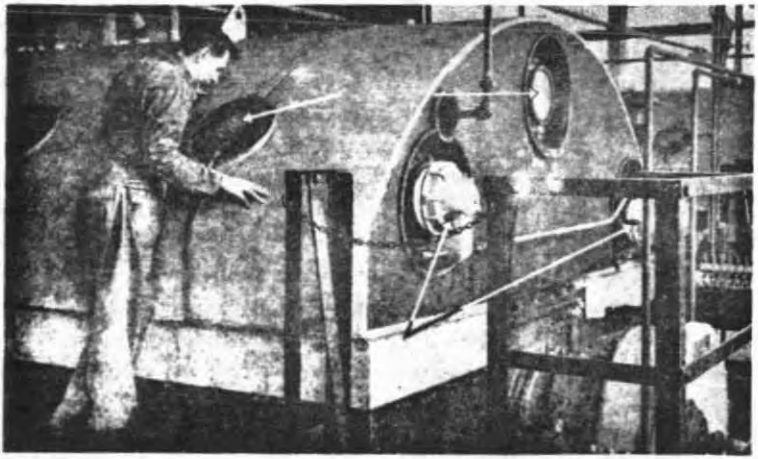
In the hydraulic presses, usually of horizontal type, are locked hundreds of canvas-covered circular metal plates and rings (Figures 16 and 17), arranged so that a space is formed between each two plates when they are pressed together. Chilled wax distillate comes into each space; the oil it contains flows out through the canvas blanket, whereas the wax remaining on the blanket is removed. The wax filter cake produced is then acid treated, and the sludge withdrawn; it is then neutralized and washed. The resultant product is *slack wax*. The slack wax is slowly melted and charged into sweat ovens where it is chilled to solidify it somewhat, and then is slowly heated. If oil and low-melting waxes drain away from the slack wax during the sweating operation and leave a high yield of wax with low oil content, the slack wax is "sweatable;" otherwise it is "unsweatable." Slack wax is marketed as such to a limited extent. A product containing about 19 per cent of oil has been marketed as a "luster cleaner."

Several samples of slack wax give the following melting point characteris-



Courtesy Standard Oil Co. (N. J.)

FIGURE 16. Workman opens the plates of one of the battery of big hydraulic presses which squeeze wax from the chilled distillate as the first step in production.



Courtesy Standard Oil Co. (N. J.)

FIGURE 17. Technician watches operation of rotary vacuum filter used in paraffin wax production at a modern solvent-dewaxing plant. Flood lights mounted outside ports at the end permit study of the wax cake as it forms on the filter blanket.

tics: drop points (ASTM) 135–145°, softening point (CC&S) 112–122°, ball and ring 130–140°, Fisher-Johns spread 117–130°, maximum 135–145°F. The penetration values (100 g/5 sec/25°C) ranged between 60 and 80.

Sweat Wax

The term "sweat wax" is sometimes confused with "slack wax" from which it differs in that the *sweat wax* is a mixture of oil and paraffins of a rather limited range of melting points in the lower melting point series.

In the sweating of slack wax the oil which is drawn off contains a large quantity of wax crystals. This mixture when chilled at only a moderately low temperature will yield on sweating the paraffins of the higher melting points and a sweat oil containing crystals that melt at 60°F and also some that melt at somewhat higher and lower temperatures. Sweat wax therefore is a solid mass at 60°F or thereabouts but appears to have 60 per cent or more of oil at 80 or 90°F.

Sweat wax is used whenever it is essential to secure extreme wax penetration, as in the textile and paper industries. It is used in wax emulsion with naphtha, or without it. A mixture of 87 parts of sweat wax; 11 parts of bentonite, whiting, or other mineral filler; and 2 parts of pigment, makes a paint suitable for closing the mesh of woven fabric, imparting color, and rainproofing.

Tent cloth can be treated with sweat wax using naphtha as a carrier. In water emulsions it is of value in waterproofing krafts. Bags for holding chemicals can be prevented from rotting by weaving the material with some form of scale wax or sweat wax treated thread.

Intermediate Paraffin Waxes

Scale wax can be considered a paraffin wax intermediate between softer waxes, such as slack wax, and the harder paraffines. It is derived by a process of sweating the greater part of oil from slack wax. Grades of crude scale wax which are marketed contain up to 6 per cent of oil. Crude scale waxes are obtainable in both yellow and white, the yellow usually containing less than 4 per cent of oil, and the white less than 2 per cent. They are produced in high as well as low melting points, although their softening points are invariably low.

Refined Scale Waxes. Ordinarily a white crude scale wax of 124–126°F melting point will contain several per cent of oil and moisture; however, a "second pudging and pressing" will bring the oil content down to below 1 per cent. Such a wax is referred to as a *special refined white scale wax*, or a *semirefined paraffine*.

Crude scale fractions when passed through bauxite beds at relatively high temperatures lose their oil content, at least down to less than 0.5

per cent, thus greatly improving the high light and stability of the scale wax.

Refined scale waxes of 126/130 grade gave the following melting points: drop 126–130°F (ASTM); softening 96–111°F (CC&S); ball & ring 126–130°F (ASTM); Fisher-Johns spread 117–122°F, maximum 126–130°F. Penetration values (100g-5 sec-25°C) were 23–33.

White scale waxes of the Atlantic Refining Company are furnished in 124–126, 128–130, and 133–135°F (AMP) grades, with an optimum expressed oil and moisture content of 0.5 per cent, and a Saybolt color of 19 average.

In the fabrication of cotton duck and canvas the thread is treated with a crude scale wax of 124–126°F (AMP) grade to impart waterproofing. A refined scale wax of 133–135°F (AMP) grade is used with material where a drier, nongreasy, finished product, which is not very susceptible to atmospheric change, is desired.

Higher-melting scale waxes are sometimes required for superior waterproofing, and to accomplish this purpose small quantities of other material, such as carnauba wax, gilsonite, or high melting asphaltume, are incorporated in the scale wax. Such adjusted scale waxes are referred to as "textile proofers." They work out economically since a thinner application will give the article the required degree of waterproofing.

Refined scale wax is used in the formulation of certain grades of artificial ceresin where lubricity to the wax is required. The use of a scale wax with much oil, or of a slack wax, may yield a product with large macrocrystals of paraffin tending to destroy the flexing or elongation. The hardness of an artificial ceresin which has been prepared by adding carnauba wax to paraffin-ozokerite mixtures can be offset by the addition of several per cent of low-melting refined scale wax.

Scale waxes of 124–126°F (AMP) grade are used in the match industry. Scale waxes of high melting point are used in the kraft paper industry, e.g., for builder's papers, cement bag stock, roofer's felt, car liners, and heavy kraft wrappings. Petrolatums of high melting point (140°F) are used in much the same way as the scale waxes for the waterproofing of kraft papers, cotton ducks, and canvas. Scale waxes of very low oil content are required in the manufacture of crayons.

Harder Paraffin Waxes

The harder paraffin waxes are referred to as *paraffines*, customarily accompanied by a designation of the melting point, such as "paraffine 128–130°F (AMP)"; or as *fully refined paraffin waxes*. The term *block paraffine* is sometimes used to designate a harder paraffin wax, one which can be molded into a hard firm block. The production of harder paraffin waxes

constitutes by far the greater proportion of the refinery output of petroleum waxes in the United States, approaching a billion pounds per year.

Slack wax which comes from the hydraulic presses, already described, contains 10 to 15 per cent oil, and this oil as well as the softer waxes must be removed in order to produce block paraffines. This is customarily done by "sweating" beyond the stage employed in producing slack wax, or intermediate waxes.

Principle of Sweating. Sweating is a process by which the oil and very soft waxes can be liquated from the firmer, harder paraffins by means of supplying heat to a previously chilled slack wax at a carefully regulated temperature. The solubility of paraffin wax in oil increases very markedly with even slight elevation of heat at temperatures 10 degrees below the melting point of the wax, thus permitting the separation of the components of slack wax by sweating. Low-melting waxes are more soluble in oil than higher-melting paraffins. Mixtures of high- and low-melting waxes have solubilities between those of the components, which makes it necessary to resweat the liquates after they have been chilled, if further recoveries of high-melting wax are to be made.

In the refining of paraffin wax, the pudged and pressed wax retains about 2 per cent of the oil at room temperature; but the amount retained at the temperature at which final sweating is carried out is too small to be detected. The presence of this small amount of oil in solution offers an explanation for some of the difficulties encountered in the separation of oil from wax. The greatest loss in wax in the sweating process occurs at the temperature at which most of the oil is removed. The wax separated from slack wax by chilling and then sweating in the initial stage is known as *scale wax*, and the by-product made up of lower-melting wax plus oil as *foots oil*. The oil sweated out in subsequent pudgings and pressings is known as *slop oil*.

Production of Paraffin Wax at the Refinery

The following process and equipment has been prescribed for the refining of block paraffine from an Eastern Texas crude wax distillate. Basically the *sweating process* follows the Henderson modification of the early methods of Price's Candle Company.

The slack wax from the chill room is melted and pumped to shallow steel pans in the *sweater house*, which houses several *sweating ovens*. The latter are well insulated rooms which accomodate one or two stacks of the long pans or trays. The pans are 8 by 20 feet and about 8 inches deep at the ends, but slope to a depth of 14 inches at the center, the pans are usually stacked eight high.

A rack of light angle or tee iron is laid in the pan and carefully leveled. A very coarse galvanized iron mesh is stretched across the rack, and over this is placed a brass wire gauze which is securely fastened to the rack, and which supports the cooling coil. There is a 2-inch space between the bottom of the pan and the gauze into

which the cold water is pumped and circulated. The melted wax is run onto the surface where it congeals to a sheet of 4 to 6 inches thickness. After solidification the pans are tilted, the oven is tightly closed, and the water run off.

The sweater oven has steam coils along the walls and under the pans for controlling the interior air temperature, and is equipped with vertical ducts between the frames to allow for air circulation. By a thermostatic regulator the temperature is raised 1 or 2 degrees F per hour, and the oil and soft wax that sweats out is drained off from time to time. The first running, or *light foots oil*, is used as a plant fuel, but the next, or *heavy foots oil* fraction, is pumped back to the wax distillate, and subsequent fractions are resweated, or used later for blending before the acid treatment. The end product is a block wax of 130–132°F melting point, which still requires a finishing treatment to remove color.

Thereafter the wax is melted and run into agitators (lead-lined and steam-jacketed), treated with strong sulfuric acid, violently agitated for 30 minutes, and settled for one hour. The acid sludge is then drawn off and the melted wax is run into another agitator, in which it is washed with hot water and then with sodium hydroxide and finally with a hot water spray. After removing traces of water by long settling, the wax is dried finally by blowing air through it.

The melted wax at this stage is not entirely colorless, and hence is run through vertical filters of hot fuller's earth. The filtered, bleached, refined wax is run into a slab mold, 40 feet or more in length, which consists of a tank-like structure having a sealed bottom, open top, and a large-size turnscrew at one end. In this housing is a series of compartments formed by *chill plates*, each plate is filled with chilled brine and connected to the other with a flexible hose so as to provide a continuous circulation. The plates are about 2 inches thick and spaced 1½ inches apart. The mold is filled with melted wax and the wax seeks its level by filling each compartment. When the wax shrinks on cooling, an extra portion of melted wax is released into the mold. After the wax is congealed, the screw at the end of the mold is unturned to loosen the plates, the plates are manually pried apart sufficiently to lift out the slabs of wax. After stripping, surplus wax is removed from the end of the slab. These slabs constitute the *fully refined paraffine* of commerce. They are 12″ x 18″ x 1½″ in size, weigh about 10 pounds each, and are packed in bags or cartons stamped with the AMP melting point. The paraffin is also packed loose or on pallets and shipped in paper-lined freight cars.

Wax Oils

Wax oils are products which are commercially available for converters who wish to employ blends of wax and oil for the impregnation of paper. These oils have been so refined that papers treated with them will impart no taste nor odor to foodstuffs. The wax oils contain 15 to 30 per cent of wax, and have a high pour point of 80 to 110°F. If used alone the paper sheet is soft and oily. Blends with petrolatum will impart less oiliness and more grease resistance for meat wrapping paper.

Two types of wax oils marketed by the Socony Mobil Oil Company (New York) known as "S/V Wax Oil No. 1" and "S/V Wax Oil No. 2" have the following physical characteristics: No. 1—gravity (API) 28.8, specific gravity ($d^{15.6}$) 0.883, bulks 7.35 lb per gal, pour point 80°F, flash point 395°F, Saybolt viscosity 126 at 100°F, color (ASTM) light 2; No. 2—gravity

(API) 32.1, specific gravity ($d^{15.6}$) 0.865, bulks 7.2 lb per gal, pour point 110°F, flash point 405°F, Saybolt viscosity 63 at 130°F, color (ASTM) light 2.

Refined Paraffin Wax

A refined mixture of associated solid paraffin hydrocarbons or paraffins is commonly designated as "paraffin wax." The word "paraffin" appears to be a French derivative of the Latin *parum*, meaning "little," and *affinis*, meaning "affinity"; in other words, a chemically inactive substance. The high-melting grades are customarily produced free from impurities and are referred to as "fully refined paraffin waxes," or by the simple designation or English term "paraffines"; for example, Asiatic *paraffines* are said to contain paraffins in the range of C_{17} to C_{34}.

Reichenbach obtained paraffin wax from wood tar in 1830, and later by the distillation of lignite, as patented by James Young in 1850. In the United States paraffin wax was first obtained from petroleum in 1868. Today, paraffin wax is produced from many "crudes" that are designated "paraffin-base oils" because of their wax content.

The wax-bearing crudes of America contain on the average less than 5 per cent of merchantable wax. Those of Galicia yield less than 3 per cent, and those of Burma 8–10 per cent. Canadian crude oils yield less than 3 per cent of paraffin wax. Much of the Russian petroleum contains no paraffin wax; an exception is the so-called "mazouts" of Northwest Caucasus which are wax-bearing. (Also see Source of Petroleum Waxes, p.. 377)

Fully Refined Paraffin Wax. The term "fully refined" is given to paraffin waxes which are water white, free from more than a mere trace of oil, odorless and tasteless, and hard or firm in consistency. The oil plus moisture content should be well within the allowable optimum of 0.5 per cent.

Fully refined paraffin wax has a friable, coarse, fibrous crystalline structure which is translucent to opaque white in appearance, particularly noticeable when a slab of the wax is broken. Microscopically its structure when crystallized from a solvent shows more or less circular or oval aggregates or platelets of cells; the fibrous characteristic in large masses appears to be due to superimposed aggregates of platelets. (Also see Crystal Habit of Paraffin Waxes, p. 405.)

Paraffines have a melting point range of 118–155°F (ASTM D-87), but ordinarily the grades melt in the range of 126–137°F, or considerably lower than microcrystalline wax. A paraffine has a color of +21 or lighter (ASTM D-156).

When melted the average grade of paraffine has a viscosity of 40–50 seconds, Saybolt at 210°F, equivalent to 4.2–7.3 centistokes, or appreciably

lower than the viscosity of microcrystalline wax. Fully refined paraffin wax (m. ca. 130°F) has a specific gravity (d^{25}) of 0.910; a flash point not less than 177°C (350°F) and usually over 400°F, and a specific heat of about 0.694 calorie per gram. Its mean refractive index (n_D) is 1.5277–1.538 at 25°C, and 1.430–1.433 at 100°C. The average paraffin wax has a molecular weight of 350–420 and contains normal hydrocarbons with a mean value of C_{25} to C_{27}. Waxes prepared from mixed base type crudes are said to have a small proportion of side-chain hydrocarbons (side-chain alkanes).

A specimen of Esso brand paraffin wax 128/130°F (ASTM) melted at 129.5°F, and had an oil content of 0.3 per cent, color +30 Saybolt, tensile strength 300 psi, modulus of rupture 400, and flexibility 0.001″ units −50.

The demand for American paraffines of the higher melting points, 130/132, 133/135, and 135/137°F AMP, has greatly increased, and the use of lower melting point paraffines has correspondingly decreased. There is only a restricted demand for paraffines melting between 143 and 150°F. These higher melting point waxes may constitute 25 per cent of the total yield of a modern refinery, and hence they are used largely to blend with paraffin waxes melting below 128°F to obtain marketable grades. A paraffine of 151°F melting point has a SUS viscosity of 43 at 210°F, a tensile strength of 151 psi at 70°F, 195 psi at 40°F, a color of 30 Saybolt, a stain pass at 135°F, and an oil content (MEK) of less than 0.5 per cent.

USP Paraffin Wax

The Pharmacopoeia of the United States of America (USP XIV)[36] defines paraffinum (paraffin wax) as "a purified mixture of solid hydrocarbons obtained from petroleum. It describes it as "a colorless, or white, more or less transparent mass, frequently showing a crystalline structure," and proceeds to describe its further characteristics. Paraffin wax, therefore, has an official or legal definition, as established by the Pure Food, Drug and Cosmetic Act of 1939, which recognizes the U. S. Pharmacopoeia.

The British Pharmacopoeia describes paraffin wax as "colorless, semi-transparent, crystalline, inodorous and tasteless, slightly greasy to the touch. Specific gravity 0.82 to 0.94 . . . It melts at 130–135°F (54.4–57.2°C) and burns with a bright flame, leaving no residue."

Paraffin wax crystals may be plate, needle, or malcrystalline. The crystals from a solvent are different from those of the melt, and are usually polygonal. The mal crystal forms as an orientation of plate and needle.

Physical Tests on Paraffin Waxes. Some of the more important physical tests on paraffin waxes include: (1) tensile strength, or the force necessary to pull the wax apart; (2) durometer hardness, or the maximum force which may be applied to a small plunger in a wax cake without forcing it further; (3) consistency, or force necessary to push a plunger into wax at a uniform rate, which is akin to viscosity; and (4) flexibility, as determined

by a bending test which measures force necessary to bend a plate of wax, and the angle to which it may be bent without cracking.

The tensile strength of paraffin waxes ranges from 60 to 320 pounds per square inch (psi); most of the commercial paraffines have a tensile strength of 180 to 210 psi.

Grades of Paraffin Wax

American Paraffin Wax. Following is a list of the grades of American paraffin wax regularly offered in the market:

Paraffin Wax	Melting Point, °F
Fully refined	120–122
	123–125
	126–130
	131–133
	133–135
	135–137
Crude scale	122–124
	124–126
	126–128

There are also special refined grades offered by a number of refining companies, such as those listed below:

Special refined	124–126
	128–130
White scale	124–126
Yellow scale	124–126
	125–127
	128–130
	135–137
	138–140
Fully refined (hard block)	138–140
	143–145

Paraffins of a specified melting point are obtainable in greatly varying tensile strengths, showing *short* or *long* characteristics as desired.

The relation between the melting point, refractive index, flow point, and hardness of each of the several grades of American paraffin wax is shown below:

M.P. (°C)	M.P. (°F)	n_D^{80}	Flow Point (°C)	Durometer Hardness 30°C	Durometer Hardness 4°C
47.8	118	1.4219	37.0	19.5	48
50.0	122	1.4253	40.5	33.0	85
55.6	132	1.4278	45.0	34.5	87
61.0	142	1.4316	48.5	34.0	88
64.0	147	—	55.5	34.0	89
70.0	158	1.4357	63.0	31.0	90
75.0	167	1.4484	59.0	30.5	91

Asiatic Paraffin Wax. The Asiatic paraffin waxes are refined from the crudes of the Netherland East Indies, which are exceptionally good in quality. The commercial grades of the Asiatic Petroleum Corporation are as follows:

	Melting Point, °F
Fully refined paraffin wax	128–130 (AMP)
	138–140
	143–145
	148–150
	158–160
	163–165
"Paraffin Wax Ceresin"	190–195 (ASTM)

The relation between the melting point, softening point, and hardness (at three different temperatures) is given below.

Grade °F Range	Actual M.P. (°F)	Softening Point (°F)	Durometer Hardness 34°F	77°F	88°F
138-140	138.0	118.0	82	77	74
143-145	144.5	124.0	83	78	75
148-150	147.5	130.0	85	81	78
158-160	160.0	132.0	92	83	80
163-165	163.0	132.5	93	85	82
190-195	196.0	170.0	100	98	97

The fully refined waxes are white in color, and the "paraffin wax ceresin" is yellow in color.

Range of Hydrocarbons in Paraffin Waxes

In the normal paraffin series the first compound that is solid at room temperature (20°C) is *n-heptadecane* which melts at 22.5°C (72.5°F). Slack wax contains paraffins from *n-heptadecane*, $C_{17}H_{36}$ upwards. In fully refined paraffin wax (128–130°F AMP) there is apparently no hydrocarbon (excluding traces of oil) below $C_{23}H_{48}$; the latter melts at 47.3°C (117.2°F). Mabery[25] in 1902 isolated six fractions in a fully refined paraffin wax and found that these ranged from $C_{23}H_{48}$ to $C_{29}H_{60}$. However, Buchler and Graves[5] isolated hydrocarbons ranging from C_{18} to C_{32} in a paraffin wax (from Wyoming distillates) that perhaps was not as close a cut as that of Mabery. The softening point of a fully refined paraffin wax (128/130°-AMP) usually approaches 36.7°C (117.2°F), indicating the presence of either a normal C_{29} hydrocarbon, or much more likely branched-chain hydrocarbons of a higher molecular weight, such as *2-methyl tricosane* ($C_{24}H_{50}$, m. 37.6°C), and/or 2-2-dimethylcosane ($C_{24}H_{50}$, m. 34.8°C).

Carpenter[6] had found in wax from Burma crude, hydrocarbons from C_{21}

to C_{34}, in which isomers of different melting point were noted from the same molecular weight. Krafft[24] investigated the hydrocarbon composition of a specimen of hard paraffin wax obtained from Saxon brown coal. The specimen had a melting point of 80°C (176°F). In this classical investigation he fractionated the wax in the vacuum of a cathode light, employing a distillation apparatus of special construction, which enabled him to distill the hydrocarbons at a pressure approaching 0.1 mm. In this manner he obtained a series of 35 fractions, comprising a complete series of hydrocarbons ranging from C_{19} (m. 31.8–32°C, 89.6°F) to C_{30} (m. 76°C, 168.8°F), identified by their molecular weights. He also recognized the presence of two or three additional higher homologs as well as small amounts of C_{15}, C_{16}, C_{17}, and C_{18} normal hydrocarbons, and olefins.

In his studies of paraffin wax hydrocarbons Mazee [*J. Inst. Petroleum*, 35, 97–102 (1949)] found that *n*-$C_{21}H_{44}$ and *n*-$C_{23}H_{48}$ form a continuous series of solid solutions. *n*-$C_{21}H_{44}$ and *n*-$C_{31}H_{64}$ form an eutectic containing 96 mol per cent of *n*-$C_{21}H_{44}$ at 40°C (104°F); the mixtures start to melt at this temperature. A mixture of *n*-$C_{24}H_{50}$ and 13-methylpentacosane also gave a binary system with an eutectic of 8.5 mol per cent of the former melting at 28°C (82.4°F). On the basis of these phenomena a hypothesis is formulated on the structure of commercial paraffin waxes.

Paraffin waxes comprise primarily straight-chain molecules with a relatively small proportion of branched or isoparaffinic material. The branched chain contains but one carbon atom and is located near one end of the main chain. Francis, Watkins, and Wallingford[15] found that the C_{32} and C_{31} hydrocarbons isolated from a paraffin wax (m. 55°C) distilled from Scottish shale did not metch *n-dotriacontane* and *n-hentriacontane*, and were evidently branched chain.

Crystal Habit of Paraffin Waxes

Investigators have studied the crystal pattern of paraffin wax from xylene and other types of solvents. Solid paraffins crystallize either in *plates* or in *needles*, the crystal habit depending upon the crystallographic behavior of the individual hydrocarbons, and the conditions under which crystallization is effected. Many of the hydrocarbons of which paraffin wax is composited undergo changes in crystal form in cooling. For example, heneicosane $C_{21}H_{44}$ (m. 40.3°C) when melted and cooled to 32.0–32.7°C, changes to a hexagonal form. Minchin[31] in his study of the hydrocarbons of Asiatic waxes found that all paraffins in the range of C_{17} to C_{34} exist (near the melting point) in a form suggesting closely packed hexagonal pencils, "the transparent rotating vertical rotating form." On cooling the form changes to the "opaque non-rotating vertical form," and this may be immediately followed by the "opaque (nonrotating) tilted form." These transitions are

reversible. Minchin also postulated a fourth form with a more tilted chain for crystals from C_{28} on.

Tetracosane, $C_{24}H_{50}$ (m. 50.7°C), has three stable modifications—hexagonal at 46.5°C, monoclinic at 42°C, and triclinic at room temperature, according to Mazee[29]. Rhodes and his associates[40] were inclined to believe that needles were "rolled up plates." They based their findings on samples of paraffin prepared from the slack wax [m. 50–51°C (122–121°F)] from Pennsylvania crude petroleum. It has also been postulated by others that the needles are normal hydrocarbons which are a continuous chain of plates. The change from the high- to the low-temperature stable form takes place at a fixed transition point. Transition effects the mechanical and electrical properties and such physical properties as coefficient of expansion, density, and solubility. Hardness is greatly increased by increased purification. Minchin found that *n*-paraffin mixtures showed a peak cone hardness over a setting range from 57.6 to 61.5°C (135.7–142.7°F), which may be connected with polymorphism. The soft wax in paraffin waxes probably has a plasticizing effect greater than that induced by transition effects. A small amount of oil reduces the hardness to a marked degree.

By microscopic examination under polarized light, Burdet-Berthod [*Bull. assoc. franc. techniciens petrols*, No. 45, 37–42 (1938)] observed that the wax of the lighter distillates from Alsatian oil form long ribbon-like crystals whose dimensions decrease as the viscosity of the distillate increases. The wax contained in the viscous distillates is in the form of very thin plates. The lighter distillates are centrifuged; centrifuging is started the minute long needle crystals begin to appear. Before dewaxing, star-like crystals are also found in the distillate.

The technique employed by Rhodes, Mason, and Sutton[40] in determining that needles of slack wax are essentially rolled-up plates, as has been previously mentioned, required that the slack wax be separated into several fractions by sweating and that the crystals of known molecular weight be studied in their process of development, i.e., without the employment of a solvent.

The sweating was done by fitting a fine copper screen into a Büchner funnel, closing the outlet, filling it with water above the screen level, and then placing a layer of melted wax on top of the water. When the wax had soldified the water was drained and the funnel and its contents were placed in a large glass cylinder in a thermostat. The temperature was raised very slowly and the oil sweated from the wax was collected in fractions. The average molecular weight of the material in each fraction was determined by the cryoscopic method, using naphthalene as solvent. In this way they secured fractions with melting points of 110.0, 117.0, 121.8, 125.0, 129.2, and 134.0°F. The average molecular weights were 415, 403, 417, 432, 443, and 445 respectively.

The behavior of each fraction was then studied microscopically. The specimens were heated and their ratios of cooling regulated by means of an insulated hot stage.

The hot stage of an ordinary chemical microscope was electrically controlled to within 1°F and used with a microscope equipped with Nichol prisms for observation with polarized light. Photomicrographs were made of the crystals during the process of development. In every case the waxes started to solidify in small plates. On rapid cooling these plates assumed a polygonal outline, or outlines. As changes were followed under the microscope it was seen that the edges of the plates actually rolled up, and that from these rolled edges there developed needles tangent to the original plate. The needles elongated and became better defined. Finally the mass solidified completely to a coarse grained structure of plates and needles. On rapid cooling the wax consisted chiefly of fine needles with a few coarse plates. Crystallization from kerosene, acetone, or xylene may be more easily controlled. On very slow cooling plates develop for the most part with only few needles.

Use of Solvents in Microscopy of Waxes

Wax crystals are formed, according to Taub and Zweig,[45] by dissolving the wax in an appropriate solvent at the solution temperature of the wax in question and allowing the solution to cool spontaneously to room temperature. Although the waxes represent mixtures of several constituents, each wax will tend to give one or at the most two types of crystal formation. Because of the dual nature of amylamine as solvent and chemical agent, it was found very suitable for wax crystallography. Butyl alcohol was also used as a solvent. Some typical crystal formations obtained with beeswax, carnauba wax, candelilla wax, and ozocerite, using amylamine, have been described, and also some odd types of crystal formations from potassium stearate in butyl alcohol and from cerotic acid in amylamine.

For crystallizing paraffin hydrocarbons from solutions, approximately 1 ml of solvent (ethyl acetate or nitrobenzene) is placed in a 5-ml vial and enough of the wax (weighed to 0.1 mg) is added to cause slow crystallization to occur at a predetermined temperature. The solution is cooled to the cloud point temperature, and a small aliquot portion pipetted into a hanging drop slide or onto the surface of a glass microslide.

Determination of Oil Content in Paraffin Waxes

Oil content of a paraffin wax is determined by the Standard ASTM method D 721-47. This method depends upon the differential solublity of oil and wax in a given solvent and is accurate within 0.2 per cent. Less reliable is the "press" method in which a small specimen of wax is highly compressed between pads of weighed filter paper for a given length of time at a fixed temperature. The gain in weight after scraping adhering wax from the filter paper is reported as "expressible oil and water."

Diggs and Buchler[9] have attempted to determine the amount of oil in paraffine by a direct refractometer method. To do this it was necessary to isolate wax-free oil and oil-free wax from paraffines. Wax-free oil had a cold test of −22°C (−4.6°F) and an index of refraction of 1.4762 at 60°C. Oil

free wax was obtained by filtering the wax through Attapulgus filter clay which selectively absorbs the oil component from a mixture of paraffin wax and oil. A 54°C (129.2°F) melting point refined wax, after filtration, had a refractive index of 1.4361 at 60°C. If there is much oil several filtrations are needed to give a constant value. Variations of index of refraction with melting point of paraffine are given below:

Melting Point (°F)	Melting Point (°C)	Refractive Index (n_D^{60}) (after filtration to constant value)
132	55.5	1.4353–1.4361 (3 samples)
130	54	1.4352–1.4359 (4 samples)
125	51.5	1.4351 (1 sample)
122	50	1.4342–1.4348 (4 samples)

These investigators found that the method works out well for the routine checking of paraffin wax of any one refinery, but each refinery must devise its own chart on the basis of synthetic paraffin wax mixtures. For example at Casper, Wyoming, the paraffin wax of 122°F melting point gives an index of 1.4342 for 0 per cent oil, 1.4362 for 5 per cent oil, 1.4381 for 10 per cent oil, etc. The method is accurate to 0.1 per cent oil. The authors regard the method to be more accurate and much simpler than the "press" method.

Sawyer, Hunter, and Nash[48] give the following data for the refractive index of *n*-paraffins:

Carbon Atoms in Molecule	Melting Point (°C)	Melting Point (°F)	Refractive Index (n_D^{60})
21	40.5	104.9	1.4287
22	44.4	110.9	1.4305
23	47.7	117.9	1.4310
24	51.1	124.0	1.4323
25	53.8	128.8	1.4341
26	56.6	133.9	1.4355
27	59.5	139.1	1.4366
28	62.0	143.6	1.4375

The solvent-index of refraction method of determining oil in wax was devised by Wilson and Wilkin[50] of the Standard Oil Company (Indiana). The method consists essentially in dissolving a 5-gram wax sample in ethylene dichloride, cooling to about 0°F, filtering off the wax, washing, and evaporating the solvent from the filtrate plus washings. This leaves a residue containing all the oil and the small amount of low-melting wax which is soluble even at 0°F. The amount of oil present therein is determined by adding enough of a special solvent to dissolve the residue and measuring

the index of refraction, the corresponding oil content being determined by reference to a predetermined curve which the authors have given.

Residual Oil Content in Paraffines. For many industrial uses it is important that the refined paraffin wax be almost free from residual oil. "Household wax," which is used for sealing jams, jellies, etc. to prevent deterioration, and in the laundry to improve finish on ironed articles, must necessarily be practically free from oil. As an example, "Parowax" contains but 0.16 per cent oil as determined by the Wilson and Wilkin method.

Asiatic paraffin wax imported from Burma and Sumatra contained but 0.02 per cent of oil. A comparison of the various types of paraffin wax is given below:

Grade of Paraffin Wax	Per Cent of Residual Oil
White scale, ordinary	2.40–2.70
White scale, candle grade	1.20–1.50
Refined, 122°F m.p. (ASTM)	0.25–0.28
Refined, 125°F m.p. (ASTM)	0.16–0.20
Refined, 130°F m.p. (ASTM)	0.08–0.10
"Parowax"	0.16
Asiatic, 135/137°F m.p. (ASTM)	0.02

The effect of the presence of a small amount of oil in paraffin wax on the resultant tensile strength has been tabulated by Adams and Maclaren[1]. The oil-free paraffin wax was crystallized from selective solvents such as acetone and benzene.

Percentage of Oil Added	Tensile Strength (psi)	
Oil-free paraffine, m.p. 130°F	0.000	395
	0.020	300
	0.038	295
	0.154	160
	0.300	70
Oil-free paraffine, m.p. 136°F	0.000	390
	0.004	387
	0.008	347
	0.034	324
	0.068	278
	0.136	244
	0.272	176
	0.544	115

Physical Properties of Paraffin Waxes

Density of Commercial Paraffines. The density of a paraffine increases with an increase of the melting point, as shown by the figures given below for the various commercial paraffines.

	Density of Paraffines with Melting Points of				
At	121° F	126° F	131° F	136° F	141° F
34°F	0.906	0.915 (35°)	0.917	0.922	0.922
45°F	0.903	0.911 (50°)	0.914 (50°)	0.919	0.919
57°F	0.897	0.909 (59°)	0.910 (59°)	0.914	0.915
80°F	0.872 (83°)	0.897	0.902	0.911	0.905 (83°)
100°F	0.849	0.873	0.877	0.896 (95°)	0.903 (95°)
150°F	0.776 (145°)	0.775	0.780 (140°)	0.779 (145°)	0.783 (145°)
165°F	0.769	0.768 (170°)	0.774 (160°)	0.772	0.775
185°F	0.762	—	0.766 (180°)	0.765	0.769

The density curves show an extrapolation from the liquid state values, which plot a straight line, through the temperature range in which the wax is normally solidified, and is taken as representing the density of the wax if it were liquid, or in solution in oil at those temperatures. At 15°C (59°F) the observed hypothetical values were found to be in good agreement with those calculated from the equation of Traube

$$d = \frac{M}{\Sigma Av + 25.9}$$

where d is the density at 15°C, M the molecular weight, ΣAv the molecular volume (atomic volume of carbon = 9.9, hydrogen = 3.1) and 25.9 is a constant termed "CO-volume."

Molecular Weight of Commercial Paraffines. The molecular weight in relation to the ASTM melting point is given below. The molecular weights are found by the cryoscopic method using *p*-dichlorobenzene as solvent.

ASTM Melting Point		Apparent Oil	Observed Mol. Wt.	Anilin Point (°C)	Calculated Mol. Weight	Corresponding Hydrocarbon	
(°F)	(°C)					C	H
121	49.4	0.5	332	116.7	330	23.55	49.1
126	52.2	0.5	340	117.8	342	24.1	50.2
131	55.0	0.3	355	119.0	359	25.2	52.4
136	57.8	0.3	372	121.0	370	26.4	54.8
141	60.6	0.3	376	122.0	375	26.7	55.4

Mean Refractive Index of Commercial Paraffines. The mean refractive index n of the paraffines in the solid state are as follows:

	Refractive Index of Paraffines with Melting Points of				
At	121° F	126° F	131° F	136° F	141° F
32°F	1.5337	—	—	—	—
50°F	1.5306	1.5321	1.5348	1.5366	—
68°F	1.5268	1.5278	1.5305	1.5332	1.5350
77°F	1.5169	1.5256	1.5277	1.5311	1.5328
104°F	1.5040	1.5071	1.5103	1.5163	1.5241
122°F	—	—	—	1.5049	1.5087

Influence of Air on Density of Paraffine. Carpenter[6] reported as much as 12 per cent of air in an American refined wax of 132.8° F (56°C) melting point. The density of this wax in the air-free condition is given as 0.919 at 60°F (15.6°C). Page[35] has shown this figure to be unreasonably high, and has pointed out the probable values for commercial paraffines.

M. P. of Wax (°F)	d_1 Observed at 50° F	d_2 Calculated at 50° F	Volume Per Cent of Air
121	0.900	0.923	2.7
126	0.911	0.927	1.8
131	0.912	0.932	2.2
136	0.913	0.934	1.9
141	0.914	0.935	2.3

The volume per cent of air occluded (not dissolved) is derived from the equation

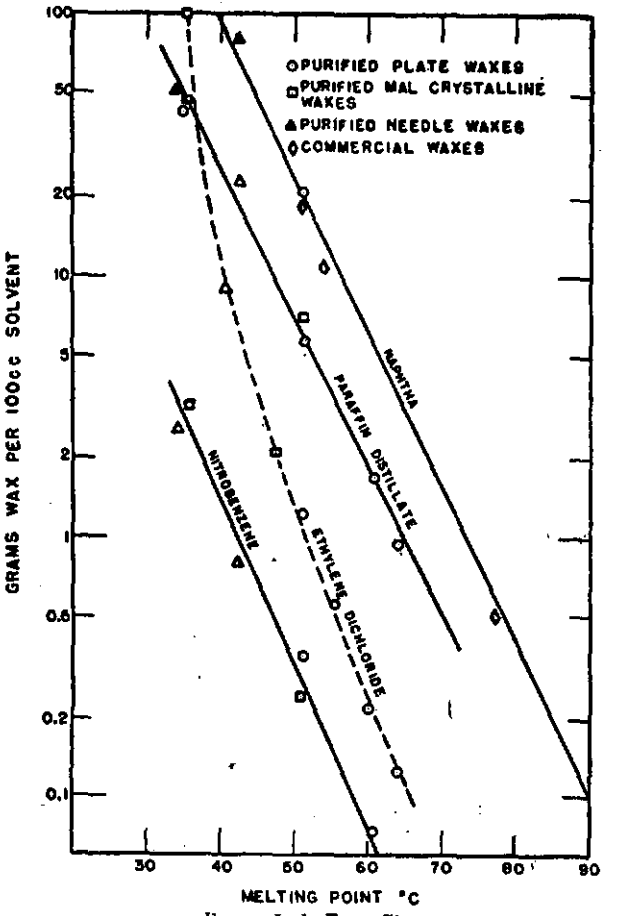
$$A = 1 - \frac{d_1}{d_2} \times 100$$

Volume Decrease of Paraffin Wax upon Solidification. Considerable importance is attached to the volume contraction of paraffin wax in the candle and other industries. Studies made of paraffin wax during solidification and crystallization have shown that (1) the volume contraction varies between 11 and 15 per cent; (2) the higher the melting point of the paraffin wax the greater the contraction; (3) the source of the paraffin wax whether from German lignite or Austrian, American, and Java petroleum, does not influence the contraction to any great extent; and (4) the contraction of mixtures of paraffin wax and stearine is greater than that of paraffin wax alone.

Specific Heat of Paraffin Wax. When solid paraffin wax is dissolved in benzene there is a volume increase but not as great as the corresponding decrease of pure liquid wax to the solid state. The solution of paraffin wax in benzene is accompanied by a decrease in temperature from which the specific heat of the wax is calculated to be 42 cal per kg of paraffin wax, agreeing closely with a direct determination of 39 cal per kg.

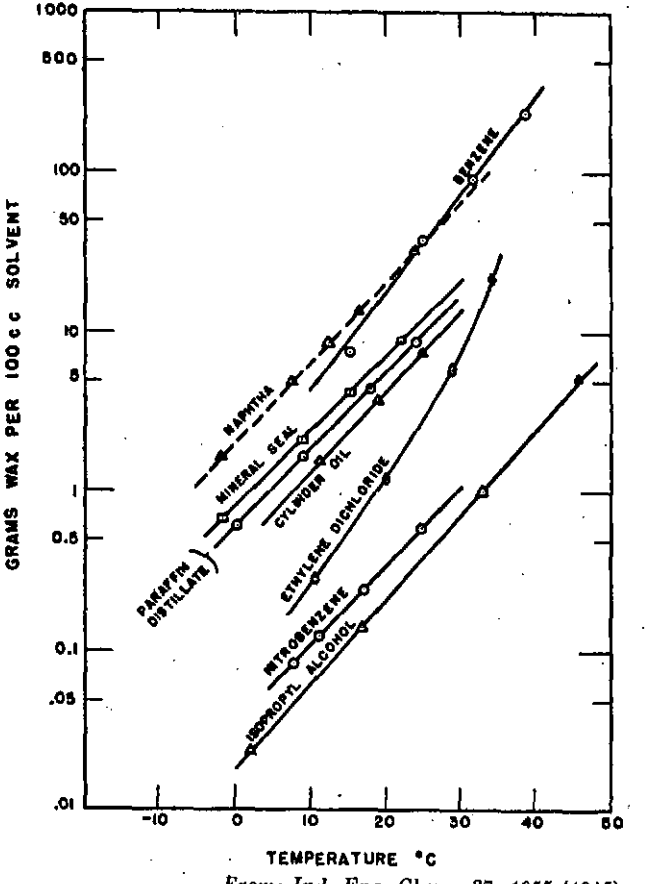
Thermal Conductivity of Paraffin Wax. The value of thermal conductivity $\times 10^4$ of paraffin wax is 6.65, compared with paper 3.27, plate glass 19.93, Norwegian pine 3.08, mahogany 3.42, ash 3.65, teak 3.97, oak 5.01, cork carpet 2.64, linoleum 3.51, leather 3.28, fire clay brick 14.35, polished clay tile 17.41, vulcanite 4.21, sulfur 6.15, and felt (green) 0.77.

Heat of Fusion of Paraffin Wax. The heat of fusion of a paraffin wax is dependent upon the range of hydrocarbons and their carbon content, and is further influenced by the chain structure, i.e., whether normal or branched. For example, if the paraffin wax has a range of normal hydro-



From: Ind. Eng. Chem., 37, 1055 (1945)

FIGURE 18. Solubility at 68°F of paraffin waxes in non-polar solvents.



From: Ind. Eng. Chem., 37, 1055 (1945)

FIGURE 18a. Solubility of purified plate wax of 125°F melting point in various solvents.

carbons between C_{21} and C_{31} the heat of fusion expressed as calories per gram would be computed from the proportional amounts of such hydrocarbons. The heat of fusion values in calories per gram for the normal alkanes are as follows: C_{21} 57.1, C_{23} 59.8, C_{24} 60.5, C_{28} 57.7, C_{30} 56.7, C_{31} 57.7, C_{35} 57.5, C_{36} 55.6, C_{43} 56.8; for the branched-chain hydrocarbons: C_{24} 48.8 for 2-methyltricosane and 47.0 for 2,2-methyldocosane, C_{26} 46.7 for 13-methylpentacosane, and 52.3 for 1-cyclooctadecane, $C_{24}H_{48}$.[29] The latent heat of fusion values of commercial paraffin waxes range from 58 to 61 calories per gram.

Petroleum waxes of microcrystalline types have a preponderance of branched-chain hydrocarbons and thus have lower heats of fusion, somewhat below 50 calories per gram, except those of very high melting point. An oil-free microcrystalline wax (190/195°F m.p.) having a preponderance of normal hydrocarbons has a heat of fusion of 57–58. The presence of naphthenes (cycloalkanes) in waxes brings about fusion points which are higher than the branched chains though lower than the normal alkanes. The heats of transition for normal alkanes have been established by Mazee:[29] C_{21} 12.3, C_{23} 16.6, C_{24} 21.0, C_{28} 15.4, C_{34} 14.4, C_{31} 15.4, C_{25} 14.9, and C_{36} 41.2 calories per gram.

Solubility of Paraffin Wax in Solvents. Fully refined paraffin wax of 128/130°F melting point has a solubility of 0.0984 gram in 100 ml of 95 per cent ethanol at 25°C. It is insoluble in 50 per cent ethanol at 25°C. The lower the melting point of a paraffin wax, the greater the solubility in an alcohol at any given temperature. The greater the chain length of the alcohol the higher its solvent power for paraffin wax.

The solubilities of various forms of paraffine at a single temperature in four solvents, and of a single paraffine at various temperatures in a number of solvents, have been given by Ferris and Cowles.[14] (See Figures 18 and 18a.)

Softening Point of Paraffin Wax. The softening point of a fully refined paraffin wax often is of use in distinguishing it from another brand of similar melting point in its composition and physical characteristics. For example,

Brand	Number of Samples	Melting Point (°F)	Softening Point (°F)	Penetration 100 g/5 sec/77°F
E	2	129.6	108.5	16.0
T	10	132.9	105.7	16.1
T	1	133.7	111.2	12.0
E	1	134.5	110.9	15.0
B	1	134.2	113.9	15.0
A	3	134.4	104.2	17.7

The softening point in relation to the melting point (ASTM) is given below for a miscellaneous lot of paraffin waxes. The letters denote products

of different refiners, which often differ in the spread between melting and softening points. The values given are average values where there is one production lot or sample.

Number of Samples	Grade Marked on Sample	Actual M.P. (°F)	Softening Pt. (°F)	Spread (°F)
1	A 101	104	78.0	26.0
1	A 111	112	86.0	26.0
1	A 121	116	89.6	26.4
3	118/120	119	93.0	26.0
18	123/125 (SO)	124	98.0	26.0
1	125/127 (CS)	126.9	102.2	24.7
1	125/127 (SVO)	125	98	27.0
20	128/130 (T)	129.7	103.1	26.6
1	128/130 (AP)	130	106	24.0
1	128/130 (SVO)	127.4	104	23.4
1	128/130 (CS)	129.7	103.1	26.6
5	131/133 (SVO)	134.3	107.9	26.3
20	133/133 (ES)	134.3	110.0	24.3
1	138/140 (Sh)	140	119.8	20.2
8	138/140 (ES)	139.3	115.9	23.4
1	138/140 (CS)	138.9	114.8	24.1
1	143/145	145	127.0	18.0
1	149/151 (ES)	150.9	131.3	19.6
1	158/160	160	132.7	27.3
1	180/185 (AP)	180	142.0	38.0

Penetration Index of Commercial Paraffin Wax. Penetration readings (mm × 10) made with a Universal penetrometer (No. 14/100 g/5 sec/x°C) are given below for fully refined paraffin waxes of the various AMP grades held at temperatures ranging from 40 to 90°C.

Temperature at		Penetration Values			
(°F)	(°C)	123/125°	128/130°	133/135°	138/140°F
40	4.4	13.5	3.0	—	—
50	10.0	14.5	5.0	3.5	—
60	15.5	16.0	7.5	5.5	4.0
70	21.1	19.5	12.0	9.5	7.5
77	25.0	23.5	16.0	13.0	11.0
80	26.7	25.5	18.5	15.0	13.0
90	32.2	59.0	42.0	28.0	23.0

The penetration values of various brands of paraffin wax may differ appreciably from the above-tabulated mean figures. For example, paraffin waxes of 128/130°F AMP will show penetration values ranging from 11.3 to 16.0 at 77°F. A paraffin wax of 132/134°F AMP will show a penetration at 77°F of 10 to 13 depending upon the source of material and mode of refining.

Durometer hardness measurements are given below for fully refined waxes of various grades.

Temperature at		Hardness (in units 0–100)			
(°F)	(°C)	123/125°	128/130°	133/135°	138/140°F
42	5.6	74.0	83.0	86.0	88.0
50	10.0	72.0	81.0	84.5	87.0
58	14.4	69.5	78.0	82.0	85.0
66	18.9	65.5	74.0	78.5	83.0
74	23.3	59.5	69.0	74.0	79.0
82	27.8	47.0	60.0	67.0	74.0

The hardness measurements below 58°F can be taken with an accuracy of only 2 to 3 points; measurements between 58 and 78°F can be made with an accuracy of 1 to 1½ points.

Fluorescence of Paraffin and Other Waxes. The fluorescent colors displayed by various kinds of waxes when subjected to the rays of black light of an ultraviolet lamp provide a partial means of identifying one wax from another. The color of the wax in the solid and liquid form is not necessarily the same, and the behavior of the waxes in solution greatly varies with the kind of solvent used[16].

Paraffin wax shows a fluorescent medium blue-green, and liquid paraffin a blue color. *Ceresin wax* shows a medium blue color, and the liquid a medium blue with a green streak. On the other hand *beeswax* shows a pale citron-yellow color, and the liquid a faint green with a blue streak. *Carnauba wax* shows a medium blue color, and in liquid form a blue-violet color. *Montan wax* gives a weak dark yellow-brown color, and the liquid a similar shade.

Alcoholic solutions of paraffin, ceresin, beeswax, or carnauba wax show no color. However, montan wax shows a blue-green color. Benzene solutions of paraffin, ceresin, or beeswax show no color. Carnauba wax shows a blue-green, and montan wax a bright blue color. Paraffin wax in ether shows no color, but ceresin wax develops a dark blue color with a violet streak, as does also beeswax, and carnauba. Montan wax gives a bright blue color. Chloroform gives a blue with green streak with paraffin, a bright blue with ceresin, a blue-green with beeswax, a bright blue with carnauba, and strong bright blue with montan wax. Carbon disulfide solutions of paraffin or ceresin give no color. A blue-green is shown by beeswax, the same with carnauba, and a gray-green with montan wax. Acetone solutions of paraffin and of ceresin yield a blue color. Beeswax gives a blue with a greenish streak, carnauba wax a blue, and montan wax a light blue. Solutions of all waxes in xylene give a bright blue color. A toluene solution of paraffin wax gives a greenish-blue color, ceresin a green, beeswax the same, carnauba wax a green-blue streak, and montan wax a blue-green streak.

"Aristowaxes"

"Aristowaxes" are fully refined paraffin waxes of relatively high melting point which possess a considerable degree of plasticity; they are recovered from high-boiling viscous lube oil distillates by a selective solvent process of the Union Oil Company of California.

The fifteen-year period preceding World War II introduced great changes in the techniques of lube oil production. The advent of large-scale high-vacuum distillation, solvent extraction, and solvent dewaxing operations resulted in the production of high-viscosity paraffinic-type oils of superior quality. The crude wax cakes containing valuable high melting point hydrocarbons, obtained as a by-product of the dewaxing operation, could not be separated or refined by the processes then in use on low-melting waxes and so they were burnt as a fuel. In 1941 the Union Oil Company of California worked out a selective solvent process in which the waxy oil is heated to above its pour point and is then pumped through double pipe scraped heat exchangers where it is cooled to a predetermined temperature at which the desired wax will have crystallized from solution. The movement of the scrapers prevents the solidification of the entire mass, a thick paste of wax crystals in oil being produced. This mixture is diluted by the addition of a relatively small amount of suitable solvent and the thin slurry formed is filtered and the wax cake produced washed with additional fresh solvent on a rotary vacuum filter. The discharged filter cake, almost completely deoiled, is slurried with fresh solvent and passed to a second rotary vacuum filter where the wax cake produced is again washed with fresh solvent. The solvent is distilled away from the wax which is then decolorized and rendered free from odor and taste by conventional means to produce fully refined paraffin wax.

"Aristowaxes" are produced at Union's Oleum, California refinery and distributed by the Petroleum Specialties, Inc., New York. They come in grades known as 143/150, 149/151, and 160/165 with physical characteristics as follows: melting points—146°, 150°, 163°F; color—25, 25, 22 (ASTM D 156-38); viscosity—44, 44, 50 (SUS sec at 210°F); specific gravity (d^{15})—0.922, 0.922, 0.933; odor and taste—none; flash point—460°, 460°, 515°F, respectively.

"Aristowaxes" are used extensively in coating paper and in the manufacture of candles. Commercial applications involve fruit wraps, bread wraps, butcher paper, laminated paper for the rustproofing of machines for shipment, wax paper for household use, and single-service milk cartons. They are also used in wax crayons, carbon paper, and wax treating electrical insulating braid, and for wax novelties and figurines, for waterproofing cellophane, etc.

"Aristowaxes" have been used by the Ordnance Department in desensi-

tizing explosives, thus rendering them safe to handle. They also act as an agent for absorbing neutrons, and are used for protecting personnel working research.

Packaging of Paraffin Wax

Paraffin wax slabs are usually 19½ inches long, 12 inches wide, and 1½ inches thick, and weight 10½ lbs each. They are packed in paper cartons, 10 slabs to a carton. The net weight of a carton of paraffin wax is somewhat over 100 lb.

Considerable savings are effected in packaging and subsequent handling by palletizing. Refiners offer a one-ton package on an expandible pallet. The slabs of wax may be set vertically to prevent blocking. One large paper cover is used to protect the wax from getting dirty. The ton package must be handled with a fork lift truck. The cost of the palletized package of wax in 1950 was 7.5¢ per lb. A carload of wax is about 30,000 lb.

Very large users of wax have the paraffin wax from the refinery delivered to them in liquid form. The molten wax is transported in a heated tank car or truck, and upon its arrival the wax (at 160°F) is pumped through a 4-inch traced and insulated pipe, into coil-heated insulated steel storage tanks, usually large enough to hold 50,000 pounds or more of wax, from which the wax may be pumped by adjustable-stroke proportioning pumps through pipes electrically heated to the manufacturing operation in which paraffin wax is used.

In 1951 the price of paraffin wax of 131–132°F melting point was about 7.1¢ per lb in full carload lots, to which 1.1¢ per lb was added to the posted price for cost of packaging.

PETROLATUM

Petrolatum—Technical

The high-viscosity lubricating oil fraction (*lube distillate*) from paraffin-base crudes contains minute crystalline types of waxes which with occluded oil constitute *petrolatum*. This fraction may be either an overhead or residual depending on the crude from which it is reduced; it has a pour point of 95 to 110°F. The lube distillate, or high-viscosity cylinder oil, is put in solution with about 65 per cent of naphtha to reduce its viscosity for clay filtering, and the filtered oil is then dewaxed.

In the process of dewaxing, the petrolatum wax is removed in petrolatum which contains upward of 25 per cent of microcrystalline wax. Dewaxing is conducted in a large storage tank equipped with cooling coils and the oil solution chilled to minus 10°F, and allowed to stand. The upper layer forms the "bright stock" solution used to produce lubricating oil upon removal of the naphtha.

A lower pour point stock (25–30°F) is obtained by mechanical separation, using a Sharples centrifuge operating at 18,000 rpm to separate the heavier *petrolatum* from the oil solution. Hot water is used to wash the petrolatum into a separator tank where the water is removed. Since the petrolatum contains some naphtha this must be removed by a drying still. The petrolatum is of a crude yellow grade with a melting point of 130 to 135°F, and has a dielectric constant of 1.90. It is used in printing inks, carbon papers, etc. For pharmaceutical uses the petrolatum needs considerable refinement (see Petroleum Jelly).

Petroleum Jelly

Petroleum jelly (petrolatum USP) is a refined petrolatum prepared from "reduced oil," that is, crude oils such as Appalachian and Mid-Continent, from which the lighter fractions have been removed by distillation, usually with aid of steam admixed with the vapors to produce low pressure and facilitate rectification. These lighter fractions include the *paraffin distillate.* Reducing is carried out under the diminished pressure by what is known as the "vacuum process," in which the heat is not directly applied to the still bottom, but by means of coils of pipe, through which superheated steam is passed. These reduced oils can be brought to 338°C (640°F) fire-test without acquiring any pyrogenous odor. They are then filtered through bone black, in chambers kept at 43 to 54°C (110–130°F), or occasionally higher, to give the greenish-red fluorescent "cylinder stock" that is valued as a lubricant. Crude oil tank residues are purified in a similar manner.

Before chilling to remove the petrolatum, or petroleum jelly, the cylinder stock is placed in solution with naphtha in proportions of 30-40 per cent of stock and 70–60 per cent of naphtha; the resulting gravity of the mixture is from 43 to 46 API[8]. It is imperative that the stock and naphtha be charged into the tanks at 90 to 100°F. In the cold settling procedure the temperature is brought down to 8 or 10°F by means of cold brine coils to effect a settling and accumulation of petrolatum at the bottom of the tank in 24 hours' time. The stock is then pumped off through suction lines leaving the petrolatum which is drawn or pumped off from the bottom.

The petrolatum after decoloration by filtration through batteries of clay and bone black filters, is graded as to cut or color, and the naphtha must be removed by pipe still. The colors grade from snow white through orange to a deep amber, and are further classified as to melting point. Melting points are determined by ASTM D 127–30 procedure, a method commonly employed for greases. The petroleum jelly is adjusted with white mineral oil to give it the proper viscosity for *"Vaseline,"* and the darker higher-melting grades are merchantable as *"Cosmoline"* for industrial use. Petrolatum, rectified from American petroleum, was first produced by Chese-

brough. "Vaseline," acording to the Metayer (German) patent[80] in 1911 was obtained by the filtration, in filter batteries, of the naphtha oils, or the residues of crude petroleum; these oils or residues are filtered and decolorized by successive treatment with reagents such as clay, charcoal, animal charcoal, etc.

The cold settling process has been superceded to a great extent by the Sharples centrifuge machine, since the gravity force of separation of petrolatum is vastly multiplied in the centrifuge. The construction of a Sharples centrifuge is such that there are continuously flowing through and out of the machine, two layers, one of bright oil and another of compressed *petrolatum*. The chilled mixture (minus 10°F) of naphtha and cylinder stock is fed into the bottom of the bowl. The petrolatum, being heavier than the dilute oil, is thrown to the outside of the bowl and is held there in a layer. Water at about 63°C (145°F) for use as a carrier liquid is jetted into the top of the bowl, which is the point of wax discharge. The water melts the wax so that it flows freely as a liquid to a compartment run tank where the wax and water are separated by gravity, the wax flowing to one compartment from which it is pumped to storage.

Artificial and natural vaselines may be distinguished by the following method. Three grams of vaseline are dissolved in 20 ml of ether; after adding 100 ml of 95 per cent ethanol the mixture is filtered and the precipitate which remains on the filter is melted and examined in a Zeiss butyrorefractometer at 65°C. Natural vaselines give values of n which are always greater than 60, whereas the n values for artificial vaseline do not usually exceed 20; intermediate values would be found for mixtures. Vaseline should dissolve freely in warm ether giving a clear solution exhibiting a strong blue fluorescence, and the liquid should not become more than slightly turbid in cooling.

Petrolatum contains hydrocarbons of the paraffin series such as *hexadecane*, *heptadecane*, *octadecane*, etc., probably up to *dotriacontane*, together with hydrocarbons of the olefin series, *cetane*, *heptadecene*, *octadecene*, etc. These olefin hydrocarbons are less concrete than the corresponding paraffins, and give petrolatum its oleaginous characteristics. Virgin amorphous petroleum wax and distillation residues are known to contain a fairly large proportion of *isoparaffins* of somewhat varying side chain length, although the *normal paraffins* greatly predominate in much smaller size crystals than in paraffin wax.

Petrolatum (USP) has a specific gravity of not less than 0.815 nor more than 0.865 at 60°C. It is insoluble in water; scantly soluble in cold or hot alcohol, but soluble in absolute ethanol, and readily soluble in ether, chloroform, turpentine, petroleum benzin, benzene, and fixed or volatile oils. It melts between 36 and 60°C. The various grades of petrolatum (petroleum jelly) marketed for pharmaceutical and cosmetic use are designated as to melting point, consistency, and color. For example an "extra light amber,"

35Y-2R on the Lovibond scale for ½-inch cell, may have a Saybolt melting point of 112/122°F, and an ASTM consistency of 170/220. Industrial users also examine the petrolatum for fiber characteristics. The medium-long fiber grades are generally preferred to those of either short or long fiber. Snow-white petrolatum has a Lovibond color of ¼ Y on the Lovibond scale, a melting point of 125/130°F, and an ASTM consistency of 185/200.

"Parmos" are USP grades of petrolatums. They are graded as to fiber, consistency, and melting point. Medium-to-long fiber is desired for most pharmaceutical and cosmetic use. Unusually long fiber tends to produce stringy, sticky compositions. As the other extreme, short-fiber petrolatum produces unguents thin in body. The fiber characteristic is determined by the proper selection of raw material and the mode of refining. Consistency is determined by penetration test; melting point is only of secondary importance. "Snow White Parmo 2-F" and "Yellow Parmo 4-F" make up a group characterized by low melting point (106/114°F, Saybolt) and soft consistency. They spread easily and lend themselves to repackaging in tubes or jars. These grades should be used when solid ingredients are present in large quantity in a formula requiring a petrolatum base. A second group of "Parmos" possesses medium consistency and melting point (110/122°F); these are widely used in pharmaceutical and cosmetic manufacture. "Snow White Parmo 1" which stands alone has a medium consistency and high melting point, namely 128/130°F. It is the whitest shade of petrolatum obtainable, and is used in formulations containing large quantities of liquid ingredients. It serves well as a plasticizer for hard waxes.

White Oil

The first white oil used in cosmetics was known as "Russian White Oil." It was first refined at Riga in 1895 by a small refinery, and exported to the United States and elsewhere for use in medicine, cosmetics, etc. It was not until 1915 that white mineral oil was manufactured in the United States. Unlike other mineral oils it is free from unsaturated hydrocarbons, as well as being free from color, odor, and taste. The unsaturated hydrocarbons are removed by the refiner with fuming sulfuric acid. Further than that the oil is alkali neutralized, washed, and percolated through a suitable adsorptive filter medium. *White oil* is also referred to in the technical literature as *liquid paraffin*, and *liquid petrolatum*, It is nearly free from fluorescence; it is miscible with most fixed oils, but not with castor oil. It has a kinematic viscosity of not less than 38.1 centistokes at 37.5°C. Aside from the main USP grades, technical grades of white oil are marketed.

White oils are used in various cosmetic creams, liquid skin preparations, hair preparations, dentifrices, and shaving creams; as dividers in making various doughs for meat hooks; for oiling eggs; for impregnating fruit wrap tissue, butchers paper, and carbon paper; as a rayon film lubricant; for

oiling wool yarn; in tobacco, insect and horticultural sprays, and ethyl cellulose-base coatings for metals; in Cottrell precipitators; and in the plastics industries.

MICROCRYSTALLINE WAXES

A microcrystalline petroleum wax is characterized not only by its microcrystalline structure but by its very high average molecular weight, manifested by a much higher viscosity than that of paraffin wax. It is customary to refer to the wax as "microcrystalline wax." In the refining of crude oil there is obtained, aside from the light ends and "lube distillate," what is known as "wax distillate," the source of refined paraffine, and "residual oil," the source of one type of microcrystalline wax.

Microcrystalline waxes are obtained as by-products from (a) the dewaxing of "lube oil raffinates," (b) the deoiling of petrolatum produced from deasphaltic residual oil, or (c) the deasphalting and deoiling of settlings of tanks holding crude oil in the oil field. These types of microcrystalline waxes are sometimes referred to as "micro wax," "petrolatum wax," and "petroleum ceresin" respectively.

Microcrystalline waxes were first produced in 1925 by the Indiana Standard Oil Company at Casper, Wyoming. These waxes were called "amorphous waxes," because of their amorphoid structure; they melted within the range of 150 to 170°F, were moderately soft, contained an appreciable amount of occluded oil, and were sticky. A number of years later microcrystalline waxes (petroleum ceresin type) were produced from "tank bottoms," that is, the discarded settlings of crude oil. Such waxes are of 170–195°F melting point, relatively hard, contain very little oil when properly refined, and are almost free from stickiness.

In the continuous-type process of refining of petroleum (see p. 378) the by-product known as "slop oil," formerly considered of little or no value, is reported to be a source of microcrystalline wax of an amorphoid structure. The slop oil is the residual oil left upon removal of the "lube distillate," and the wax can be separated by recrystallization and settlings from naphtha solution at reduced temperatures.

The oil-binding and oil retention properties of microcrystalline waxes are pronounced, and since the waxes must be freed from the residual heavy oils in order to furnish products usable for special applications, separation is usually effected by means of selective solvents. Diluents which have selective solvent properties are frequently mixtures of the polar and nonpolar type (see p. 422).

Solvent Dewaxing Processes for Microcrystalline Wax

Solvents for effectively separating the microcrystalline waxes vary with refinery methods and the character of the feed stock. Polar solvents are

generally used with nonpolar solvents in the dewaxing of heavy wax-bearing oils of cylinder stock viscosity. Specific nonpolar solvents may be chosen from the chlorinated solvents, diluted with benzene, toluene, or naphtha as the case may economically require; and polar solvents from acetone, methyl ethyl ketone (MEK), etc. Benzene and toluene are excellent solvents for the oil but they are also good solvents for the wax. For this reason, if no antisolvent were employed, the dewaxing temperature differential (temperatures) would be high. Benzene is less desirable than toluene because of its high melting point (4°C) when operating at chill temperatures and its somewhat higher cost. Acetone and MEK are called antisolvents because they do not readily mix with the oil.

The purpose of the polar solvent, such as MEK, may be summed up as follows: (1) to aid in the formation of more definite microcrystals, (2) to increase the rapidity of filtration, (3) to make it possible to precipitate the wax at a higher chill temperature, and (4) to reduce the amount of total diluent needed to effect the proper separation. The ration of MEK to benzene-toluene is controlled by (1) the structure of the wax removed and (2) the amount of ketone which can be tolerated without dissolving enough oil to precipitate a significant amount with the wax.

The oil is mixed with about 3 to 4 parts of combined polar and nonpolar solvent or a proportion of the latter to prevent separation of the oil from the mixture at a predetermined chill temperature, say −10°F. The mixture is then chilled and the precipitated wax removed.

Specific solvents of the nonpolar type referred to in improved dewaxing technology include dichloroethane, dichloropropane, dichloroethylene[20], trichloroethylene, and other halogenated organic compounds. Other solvents are nitrobenzene, aniline, benzophenone, etc. Such solvents are also customarily diluted with naphthas or with benzene-toluene.

Poell[37] claims that with the combination of the wax precipitors 1,1-dichloroethane and 1,2-dichloroethane, a solvent-precipitation couple has thus been found for centrifugal dewaxing which must be considered fully equivalent to the solvent-precipitor couple of acetone-benzol extensively used for dewaxing with filtration. At every ratio of admixture the dichloroethanes (1,1- and 1,2-) yield a large-scale, well crystallized paraffin wax precipitate which can easily and quickly be separated by either centrifuging or filtration. Dewaxing at extremely low temperatures does not present any difficulty as in these cases a further addition of 1,1-dichloroethane is sufficient to obtain a pure wax precipitate.

Govers[18] found that the rate of filtration can be substantially increased by use of bis(2-chloroethyl) ether ("Chlorex") as the nonpolar solvent, followed by chilling to precipitate the wax constituents (of higher melting points), and filtering in the presence of a polar substance of the character

of liquid SO_2, acetone, and MEK to cause further precipitation of the wax; the polar substance comprises about 5 to 10 per cent by volume of the mixture of wax-bearing oil and nonpolar diluent. The solvent is recovered after the filtrate has been dewaxed. Chlorinated solvents present certain valuable characteristics such as their high specific gravity, which permits an easy separation of the wax and oil layers by centrifuging. The solvents used may be a single solvent as represented by trichloroethylene or a mixture of solvents, like ethylene dichloride (2,2-dichloroethyl ether) and benzene.

Dennis *et al.* have found that residual lubricating-oil stock is dewaxed upon contact with a urea solution in a mixture of cresylic acids at about 125°F. A crystalline complex of the urea and wax, or urea adduct, is separated from the oil by filtration or other suitable means. The dewaxing process may follow a propane-deasphalting step in which the cresylic acids are left in the oil. In practice, 1 part by weight of lube oil stock is mixed with 1.9 parts of cresylic acids and 0.8 part of urea at 125°F for a half-hour. Naphtha ($b_{200-300°F}$) is added, and the complex of urea and wax is filtered off, washed with naphtha, and decomposed with water at 150°F. The product obtained consists of a mixture of paraffin and microcrystalline waxes, or so-called "micro waxes." [Dennis, F. L., *et al.* (Socony Vacuum Oil Co.), U. S. Patent 2,642,379 (1953); also cf. Fetterly, L. C. (Shell Development Co.), U. S. Patent 2,642,377 (1953).]

Petrolatum Wax

In 1936 Diggs, Beard, and Page[9] described an adhesive electrical insulating *petrolatum wax* which they had prepared from Salt Creek crude oil. It had a melting point of about 158/160°F (maximum) and was found to have the property of adhering to polished surfaces at 32°F without contracting. They deemed it suitable for insulating metal wires, etc. This wax was the forerunner of the soft, more or less sticky microcrystalline waxes of similar melting point that are used in manufacturing industries where such physical characteristics are essential.

Petrolatum wax, or "crude petrolatum wax" as it is also called, is essentially a microcrystalline wax which contains 10 per cent of oil, or somewhat more or less. It is obtained from acid-treated petrolatum stock, containing a fairly high percentage of wax, by treatment with naphtha and centrifugation of the solution to remove excess oil[21]. This wax, which contains more than 10 per cent of oil, may again be put into solution and recentrifuged to further reduce the oil content.

A method of preparing the crude wax is that of Diggs, Beard, and Page[9], in which the "bottoms" or residues of the still are treated with sulfuric acid to remove asphaltic material; the oil is neutralized, filtred, and chilled

to a temperature near freezing, whereupon the petrolatum wax precipitates. The latter is dissolved in ethylene dichloride or in naphtha, and cooled to a temperature at which the high-melting crystalline fraction precipitates, usually at 100 to 70°F. This paraffin is removed (worked up separately) and the resulting solution comprising the microcrystalline wax is cooled to below 40°F to precipitate out the adhesive wax fraction (petrolatum wax), which is separated and ready for use. The petrolatum wax may, however, be redissolved in a specific solvent and reprecipitated in a paler-colored product of a somewhat sharper and higher melting point. In the method described the naphtha is of 54 API gravity and the recoveries of wax are made from a 20 per cent naphtha solution. The second centrifuging removes a wax that melts at about 147°F and possesses high adhesiveness. The adhesive wax may contain as much as 21 per cent of oil, but the oil content may be reduced by reprecipitating the fraction from naphtha, by pressing, or by any suitable means. If the oil content is reduced to about 18 per cent, the melting point is raised to 151°F. Acetone and benzene, as an azeotropic mixture, may be used advantageously instead of naphtha to reduce the oil content. The crude petrolatum wax may also be fractionated into waxes having melting points of about 165, 150–160, and 140–150°F.

A laminating microcrystalline wax has been prepared directly from crude oil. Salt Creek crude oil is reduced by the Standard Oil Company (Indiana) to 40 per cent of "bottoms," diluted with naphtha, and centrifuged to yield a yellow microcrystalline petrolatum wax, melting at 150–175°F. The wax can also be prepared by filtering the crude oil through clay, which is then exhausted with "Chlorex" or furfural.

Waxes from Petrolatum Stock

Microcrystalline waxes are recovered from the *residual oil* left upon the removal of the *heavy viscosity fraction*, or "lube distillate," which is the higher-boiling cut, after the *pressible wax distillate*, or paraffin distillate. It is also recovered directly in modern processes from the heavy viscosity fraction itself. This fraction also contains wax, but because of the minute size of its crystals does not lend itself well to separation by filter-pressing. The high-viscosity fraction is cold-settled and centrifuged, thus yielding an oily wax portion known as *petrolatum stock*, and lubricating oil. Refined *petrolatum* is obtainable from petrolatum stock, or a soft *microcrystalline wax* can be separated by recrystallization and settlings from naphtha solution at reduced temperatures (see Petrolatum, p. 417).

However, if the heavy viscosity fraction is distilled, there remains residual oil which will not distill overhead at atmospheric pressure without decomposition. The problem then becomes one of separating the asphalt, sulfur, and other impurities from the fraction's valuable oil and wax

constituents. This is done in part by treating the residual oil with sulfuric acid, or the asphalt may be recovered by one of the newer selective solvent processes. If acid-treated the residual oil is dewaxed and the petrolatum residuum is then taken up with solvent, chilled, and dewaxed; or the residual oil is put through a two-stage process in which mixed polar and nonpolar solvents are used to dewax the oil in the first stage, and the petrolatum separated by centrifuge is again taken up with an organic solvent, chilled, and centrifuged to separate *microcrystalline wax* from the slop oil which is of little value.

De-oiling Petrolatum Wax using Propane

Petrolatum produced in normal refining operations by the cold-settling or centrifuging of residual steam refined stock, or cylinder-stock distillate, is known to contain from 25 to 75 per cent of high melting point wax and 75 to 25 per cent of "bright stock." Tears[46] proposed a method of deoiling petrolatum wax using propane. The petrolatum wax of Pennsylvania crudes is treated in this manner. In the Tears process the propane is kept in a cold storage tank from which it can be drawn into an auxiliary tank, so that it can be fed with a suitable amount of petrolatum into a heater, thence to a cooler and over to a series of large drums known as "chillers" and "settlers," which are also linked up with a plentiful supply of propane. With chillers and settlers full to capacity, the liquid contained in each of three tanks to the top of the try cock may be 1800 gallons, of which 1325 gallons would constitute propane and 475, petrolatum to be stripped. The temperature is reduced to −45°F, which corresponds to atmospheric pressure. The agitation of the mixture by entry of warm and cold propane and the boiling by evaporation makes a perfectly uniform mixture from which the solid wax may be settled in an hour or two. The bright stock has good color, and a pour test of 0 to 5°F.

To remove the last traces of oil from the wax, or propane from the oil, additional adjuncts known as "wax and oil strippers," comprising a "wax stabilizer" and an "oil stabilizer" suitably equipped with steam coils, are employed. In this manner a wax of high melting point can be produced.

Precipitated residue from propane extractions are sometimes referred to as "petroleum polymer." The polymer material is black in color, has a high melting point, around 139°C (282°F), and a softening point as low as 27°C (80°F). This inexpensive material is of considerable value in laminating foil to kraft paper and large quantities are used for this purpose. It is applied at a temperature af 205°C (400°F).

Jones[22] selectively extracts the oil from a petroleum stock such as a distillate from a Mid-Continent oil by dissolving the oil content of the stock in a mixture comprising 1,1,2- or 1,1,1-trichloroethane and another

material such as trichloroethylene, dichloroethylene, benzene or naphtha, or ethylene dichloride and a propylene dichloride; the wax is removed from solution at a temperature sufficiently low to effect its precipitation.

Knowles[23] has proposed to mix the wax-bearing mineral oil with aliphatic ketones, e.g., dipropyl ketone and methyl ethyl ketone in such proportions that at −18°C the solvent action on the oil is complete, but there is substantially no solvent action on the solid waxy constituents. The mixture is chilled to effect wax separations. Knowles also advised the use of dialkyl ether, such as acetal, as a selective solvent for the same purpose. Gross and Overbaugh[19] suggested treating the wax-bearing oil with 4 parts of commercial methyl isobutyl ketone, and chilling the mixture to about −10°F to precipitate the wax and remove it.

Tank-Bottom Waxes

Some of the high-melting microcrystalline waxes are refined from the wax settlings accumulated in the storage of crude. At the bottom of an oil well in Texas or Oklahoma, the temperature of the crude oil often exceeds 140°F, and hence when the oil flows or is pumped to the surface and is collected in large tanks, its slow cooling in the tanks causes the solidification of the high-melting wax fractions which settle to the bottom. Sand, emulsified oil, asphalt, and other impurities also settle out along with the waxy fractions while the crude is stored. Obviously the "tank bottoms" must be removed from time to time so as to permit the flow of crude oil through pipelines to the refinery[7].

When the crude emulsified wax or "tank bottom" is removed from the tank by pumping, shoveling, and scraping, the emulsion must be broken. The crude wax is freed from water and dirt by settling, centrifuging, or filtering, and the dehydrated tank bottom is sent to the refinery where the crude oil is removed by distillation leaving a black wax containing about 5 per cent of asphalt. The black wax has a melting point of 180–185°F, is of plastic consistency, and has only a limited market except for refining to dark amber and lighter-colored grades.

To prepare the dark amber grade the asphalt, dirt, sulfur, and other impurities are removed by acid and clay treatment. The dark amber wax still retains 10 to 15 per cent of oil hydrocarbons of high molecular weight. Most of the occluded oil is subsequently removed by selective solvent treatment, and with additional clay treatments waxes of light colors are produced. Few crude oil refiners process their own tank bottoms; they sell them to the refiner specializing in such wax production. The preferred selective solvent for producing the less plastic, pale-colored waxes is an azeotropic benzene-acetone mixture.

Waxes of the "tank bottom" type are also blended by some refineries

with those of the "petrolatum" type to produce refined microcrystalline waxes of intermediate melting point range, and of the desired "fiber." Tank bottom waxes, with some exceptions, are not of equality to the petroleum ceresins, which are prepared from petrolatum stock by selective solvent adsorption.

Bleaching of Microcrystalline Waxes

The principle of decolorizing paraffin or petrolatum waxes is the same as that for the lower hydrocarbons, except that heat must be maintained with the waxes to keep them in a fluid state, as for example by using steam-heated filters. The percolation process is the one commonly used for the hydrocarbon waxes.

The process of bleaching wax, as originally introduced by Weingaertner[49], consisted of heating the wax above its point of fusion to 130°C, adding fuller's earth to the extent of 10 per cent, heating to 153 to 170°C, and filtering.

A light-green adsorbent phyllite, named attapulgite, occurs at Montmorillon (Vienne, France) and Attapulgus, Georgia (U. S. A.). Analyses of these clays are quite alike as shown below:

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O
Montmorillonite	53.6	10.6	6.5	0.3	4.6	2.1	0.8	0.5	11.6
Attapulgite	53.7	9.3	3.6	0.2	9.0	1.2	0.9	0.5	9.7

It is postulated that attapulgite has been formed from an alkali-magnesia mica and that its adsorbent properties are owing in part to zeolitic waters.

The clays are mined by the Floridin Company in northwest Florida, and by the Attapulgus Clay Company, Attapulgus, Georgia, the deposits being about twenty miles from each other.

Waxes such as paraffin or ceresin are customarily refined (oleum treated) before they are treated with bleaching clay. Microcrystalline waxes customarily bleached with attapulgite or other special clay may subsequently be fully bleached to a paler color by a more active or acid-treated clay of the "Tonsil" or similar type. In the case of paraffin wax the bleaching temperature is from 90 to 120°C, with ceresin and ozocerite about 180°C, and with microcrystalline waxes not less than 180°C. It takes about 30 minutes to bleach the waxes with bleaching clay. Special grades of "Tonsil"[47] are offered by the vendor for the purpose of bleaching the wax to a snow white. (Also see p. 390.)

Beeswax can be decolorized without preliminary treatment, with bleaching clays at a temperature of 90–95°C over a period of 30 minutes. When the color of a crude wax is reddish, bleaching can be aided by an activated

carbon (e.g., "Norit"). Diatomaceous earth synonymous with infusorial earth, kieselguhr, fossil flour, celite, fossilite, etc., is a filter aid and has little or no bleaching power.

Bleaching of Hydrocarbons by Alumino-silicate Gel

Hydrocarbon waxes in the liquid phase may be decolorized and deodorized by treatment with alkali-free aluminosilicate gel, or by "Silica-gel," by contact for a protracted length of time and at a temperature appreciably higher than 50°F above the melting point of the wax. This treatment is of particular value in producing anhydrous odorless hydrocarbon waxes, and can be used in conjunction with activated carbon treatment to improve decolorization.

Brands of Microcrystalline Waxes

There are numberous brands of microcrystalline waxes, and these brands differ because of the character of the raw lube or residual stock, and the method of refinement. There are gradings according to color: black, brown, dark amber, amber, pale amber, pale yellow, and white waxes. These gradings are associated with the melting points such as 160/165°F, 170/175°F, 180/185°F, and 190/195°F. Patentees in the past have associated brand names with their patent specifications. Rau[38] stated that in his composition, consisting of beeswax, amorphous petroleum wax and a wax-hardening agent, one can use "Petrowax" of the Gulf Refining Company or "Superla Wax" of the Standard Oil Company of Indiana. Aside from the color and melting point, the needle penetration value is a guide in selecting the brand of wax for a specific purpose. Waxes of 160–165°F melting point ordinarily show a penetration (100 g/5 sec/25°C) of 20 to 60, or even higher; waxes of 170–175°F grade a penetration of 10 to 24; waxes of 180–185°F grade a penetration of 8 to 20; and waxes of 190–195°F grade of 3 to 16.

"Be Square" Waxes. The Bareco Oil Company at Tulsa, Oklahoma, refines microcrystalline waxes in different melting point ranges. These comprise brands known by the trade name "Be Square," of black, amber and white colors in 170/175°F, 180/185°F, and 190/195°F melting points. The "*Be Square White*" waxes are both tasteless and odorless, and are considerably higher priced than the colored grades. The "Be Square Amber" ordinarily has an NPA color of 2, but paler colors are also produced. A wax of the snow-white crystalline type is more costly than the pale yellow, or amber type, because of the expense involved in the labor, and the loss of wax on filtering with relatively large volumes of clay.

"Crown" Waxes. The Petrolite Corporation, Ltd., Kilgore, Texas, markets under the name of "*Crown Waxes*" several types of microcrystalline petroleum waxes of 190–195°F melting point, also one having a melting

point of 195–200°F. For example, "Crown Wax 700" has a color of 2 to 2½ NPA; acid and saponification numbers nil; a molecular weight of 872; molecular structure of branched-chain paraffins in C_{50} to C_{65} range; specific gravity (d^{25}) 0.9415; viscosity SSU 210°F (ASTM D-155-45) 77.0; see softening point (CC&S) 173.0°F; penetration (100 g/5 sec/77°F) 3; refractive index ($n_D^{203°F}$) 1.4401; Conradson carbon residue 0.03 (%); and ash 0.1 per cent. The heat of fusion is given as 70.5 Btu/lb, and specific heat as 0.545 Btu/1°F/lb. "Crown Wax 1035" graded as 195/200°F melting point is of extra pale color and has a penetration of 2. It is rated as having an oil content of 0.6 whereas "Crown Wax 700" has an oil content of 2.3 per cent. "Crown Wax 200" graded as 190/195F melting point is of a brown-black color, has a penetration of 10, and contains 10 per cent of occluded oil.

"Micris" Waxes. The Commercial Oil Corporation, Warren, Pennsylvania, markets under the name of "Micris" several kinds of microcrystalline waxes including "Micris 777 Yellow." The latter is described as having a meltinz point (ASTM D 127–30) of 190°F; color-liquid NPA of 2–2½; color-solid yellow; flash, COC 580°F; viscosity SUS/210°F of 83; oil content (% ED) 0.1; stain pass at 160°F; penetration (ASTM D 5–25) 5 at 77°F, 7 at 90°F, 36 at 160°F; dielectric constant 2.06; % power factor 0.11; volume resistivity (ohm-cm × 10–12) 36.6.

"Mekon" Waxes. The Warwick Wax Company, Inc., Long Island City, New York, markets several types of microcrystalline waxes under the name of "Mekon." The "Mekon 20" series is of in black, amber, and yellow colors. "Mekon Y-20" is the yellow color, 2-2½ NPA. It has a melting point of 190–195°F, a penetration of 3, a flash of 550°F min., and fire of 575°F min. The viscosity at 210°F (ASTM 88–38) is 83–88 seconds. It is rated as being insoluble in ethanol, and in acetone. It is soluble hot in benzene, dioxane, carbon tetrachloride, and kerosene; soluble hot or cold in toluene, xylene, chloroform, trichloroethylene, turpentine, VM&P naphtha; and slightly soluble hot or cold in ether.

Suggested uses for microcrystalline waxes of 190–195°F melting point are for the waxing of wooden kegs or barrels, as an antiblocking additive for use on paper coatings, and for electrical purposes since they are adaptable to use in impregnations, coatings, potting compounds, and moisture-proofing. Most often these very high melting waxes are blended with microcrystalline petroleum waxes of lower melting point for or by the industrial user.

Characteristics of Microcrystalline Waxes

Microcrystalline waxes have a high melting point and are all of about the same molecular weight. The hydrocarbons of which they are com-

posed have chains almost twice as long as those of the macrocrystalline waxes. It is believed that the chain is doubled over and somewhat intertwined with itself, which would make its effective length in some respects no longer than the paraffin chain. These amorphoid waxes, even in the higher melting points, may be quite soft and adhesive; but they may also be quite hard and firm like beeswax. In general, most of the microcrystalline waxes have a high degree of plasticity which makes them valuable for uses where plasticity and high melting point are desirable.

There are several theories with respect to the cause of the microcrystalline structure. One theory is that this structure is owing to a natural inhibitor, possibly a long-chain carbon, as may be found in asphalt. If such an inhibitor could actually be isolated it would when blended with a crystalline wax yield an amorphoid wax. Another theory is that microcrystalline waxes are associated with heavy residual stocks and cannot be separated completely from the high pour oil and therefore can form no well-defined crystals; paraffin waxes, however, are associated with only light distillates and can readily be separated as macrocrystalline types.

There is some speculation as to whether an unsaturated hydrocarbon such as $C_{34}H_{66}$ might be a factor in causing the so-called oiliness of these waxes. *Tetratriacontadiene* (prepared by the electrolysis of sodium oleate solution) and other higher homologs of the unsaturated series have been studied by Dover and Helmers[12] for the lubricating value which they give to oils. The $C_{34}H_{66}$ hydrocarbon has a melting point as low as 20.5–21°C; a density(d^{22}) of 0.8410; an iodine number of 102.5; refractive index(n_D^{20}) of 1.4655; and dielectric constant (25°C, 130 kilocycles) of 2.82. By hydrogenating the yellow paraffin using platinum oxide as a catalyst and ferrous sulfate as a promoter, a white solid paraffin, m. 71.5–72°C, which corresponds to the normal saturated paraffin, *tetratriacontane*, is formed.

Physical Constants of Microcrystalline Waxes

A microcrystalline wax derived from petroleum may be defined as a solid hydrocarbon mixture, of average molecular weight range of 490 to 800, considerably higher than that of paraffin wax, which is 350 to 420. The viscosity (SUS at 210°F) of a microcrystalline wax is within the range of 45 to 120 seconds. The lower limit corresponds to 5.75 and the upper to 25.1 centistokes at 210°F. The penetration value (ASTM) is of wide variation, namely 3 to 33, although sticky oily laminating waxes are encountered with as high a penetration as 60. Microcrystalline waxes in the range of 160 to 190°F melting point are for the most part moderately plastic; the penetration values usually range from 8 to 30. Waxes of 190/195°F or higher melting point are less plastic, and some are brittle. They have a penetration value below 10.

Microcrystalline waxes contain from 0.1 to 13 per cent of occluded oil. Waxes with a penetration (ASTM) below 10 usually have an oil content of 1.0 to 4.0 per cent; if of penetration 10 to 20 an oil content of 3.0 to 5.8 per cent; and if of penetration 20 to 30 an oil content of 5.5 to 10.5 per cent. The refractive indices (n_D^{30}) of microcrystalline waxes range from 1.4240 to 1.4520; and the refractive indices (n_D^{100}) are 1.4350–1.4450, or somewhat higher than those of paraffin wax (1.4300–1.4330). The flash point of paraffin wax is 400°F minimum, whereas the flash point of microcrystalline wax is 500°F minimum. For example, a microcrystalline wax of 190/195°F M.P., yellow in color, viscosity SUS/210°F (ASTM D 446–39) 83 to 86, penetration (ASTM D 5–25) at 25° (77°F) 5 to 6, had a flash point, COC (ASTM D 92–46), of 580°F.

The pronounced increase in penetration with increase in temperature is shown by the following example. A brand of microcrystalline wax known as "Micris 777 Yellow" of the Commerce Oil Corporation, Warren, Pennsylvania, had a penetration of 5 at 77°F, 7 at 90°F, 9 at 100°F, 15 at 130°F, and 36 at 160°F. It was reported to have the following electrical properties at 100°C (212°F): resistivity (ohm-cm $\times 10^{12}$) 36.6, power factor 0.0011, and dielectric constant 2.06. Its oil content is said to be only 0.1 per cent. The dielectric constant of "Crown 1035" microcrystalline wax (m. 190.2°C)

TABLE 66. PROPERTIES OF MICROCRYSTALLINE WAXES

M.P.	Color	Oil Content	Designation	ASTM Penetration	Viscosity SUS at 210°F	Gravity API	Molecular Weight	Refractive Index @ 80°C	Distillation	
									5% Pt.	O.H. @ 620°F
147	Amber	1.3%	A	19	92.2	34.2	530	1.4503	450	51.5%
166	Yellow	2.4	E	8	63.2	38.3	565	1.4403	468	77.0
173	Yellow	2.5	I	10	52.9	39.2	530	1.4240	489	93.0
172	Pale yellow	4.0	G	13	65.6	37.4	510	1.4450	456	62.5
196	Amber	4.5	J	3	79.3	36.4	610	1.4330	475	54.0
158	Brown	5.2	B	18	65.3	36.1	655	1.4469	425	67.0
173	Amber	5.7	H	16	75.2	35.7	640	1.4490	432	61.5
161	White	5.8	D	21	50.2	39.0	545	1.4408	456	FBP 58.0
161	Amber	8.6	C	29	78.2	34.5	490	1.4518	460	59.0
167	Amber	10.5	F	31	65.8	36.1	610	1.4470	430	68.0

A, B, C, E, F, G, are residual waxes.

A is Penna.-type crude oil, good sealing power and good flexing.

B, C, and F are residual waxes from Mid-Continent-type crude oil.

D is a high grade of motor oil wax. Its lower viscosity at 210°F is noteworthy as indicating a content of crystalline wax. This is also indicated by a higher gravity and a narrow, lower boiling range.

E may be a tank-bottom wax.

H, I, and J are typical of refined tank-bottom waxes.

of the Petrolite Corporation, Kilgore, Texas, was reported as 2.46 at 80°C, and that of "Crown 500" (m. 184.5°C) as 2.38. The potential breakdown (v/mil) of these waxes was reported as 675 and 420 respectively at 80°C.

The oil content of a microcrystalline wax is measured to some extent by the temperature at which the wax compressed in a thin layer between the folds of a nonsulfite paper will cause the paper to stain. For example, a wax of 190/195°F (AMP) may pass the staining test at 145 to 160°F.

A microcrystalline wax of 190°F melting point and of a highly plastic nature, and which will not stain uncoated sulfite paper, yet which contains 10 per cent of free oil, is prepared by taking a deoiled wax residue and distilling it at reduced pressure, when a cut is taken off at a predetermined viscosity, and then adding 10 per cent of a 26° gravity oil. The object is to secure a stain-free wax of high penetration value (15 to 20 plus), but yet of very high melting point.

Suggested use for such a wax is in the lamination of glassine or other sheet material in preparing wraps for cakes, which will be free from oil stains when subjected to the warmth of packaging, etc.

Specific Gravity of the Microcrystalline Waxes. The specific gravity of microcrystalline petroleum wax is quite different in the molten state from that of the solid state, as is also true of other waxes. Measurements made of the petroleum ceresin, "Petrosene A" (m. 163.8°F, 73.2°C) of the specific gravity based upon water at 15°C, are here tabulated.

	°F	°C	Specific Gravity
In Solid State	44	6.7	0.9343
	60	15.6	0.9294*
	80½	26.9	0.9236
	127	52.8	0.8921
	160	71.1	0.8300*
In Liquid State	170	76.7	0.8025
	180	82.2	0.7999
	200	93.3	0.7935
	212	100.0	0.7890
	240	115.6	0.7805
	280	137.8	0.7610
	320	160.6	0.7535
	360	182.2	0.7410
	400	204.4	0.7380
	438	225.6	0.7140

* Computed value.

The specific gravity of the molten wax increases fairly rapidly as the wax cools down to the approaching resolidification point. During the critical stage of solidification or until the soft wax reaches a temperature low enough to become a uniform solid, there is a pronounced increase in the gravity.

On lowering the temperature further, there is a less marked drop in the gravity of the wax is the perfectly solid state.

Coefficient of Expansion of Microcrystalline Waxes. The coefficient of expansion of a wax can be determined from the change in specific gravity with change in temperature, e.g., by the formula $d':d = 1:1 - Dt$, where d = density of body at initial temperature, d' = density of body at observation temperature, and t = difference between the initial and observation temperatures. From the above equation we arrive at the formula

$$D = \frac{d - d'}{td'}$$

Using this method for determinations of the density of wax in the liquid state by a Westphal balance, there results a cubical expansion figure of 0.0008138 per 1°C (0.0004521 per 1°F) for one brand of petroleum ceresin known as "Petrosene A," and a figure of 0.0007911 per 1°C (0.0004395 per 1°F) for another brand[48].

Hardness of Commercial Microcrystalline Waxes

	Melting Point (°F)	Softening Point (°F)	Max. Oil Content (%)	Durometer Hardness 34°F	Durometer Hardness 84°F
"Petrowax"	157–159	116–120	13	56	20
"Petrosene A"	167–171	139–144	7½	75	42
White Mineral	163–168	130–136	4–5	78	52
Pale Yellow	185–188	166–170	5–7	94	80

Penetration Indices of Microcrystalline Waxes. Penetrations are made on the microcrystalline waxes with a number 14 penetrometer needle (0.14 mm diameter of the truncated blunt point), and a 100-gram top weight operating for 5 seconds, with the specimen at 25°C (77°F). For very hard waxes a 200-gram top weight is used.

Specimen Labeled	Melting Point (ASTM Drop) °C	Melting Point (ASTM Drop) °F	Penetration Reading (100 g/5 sec/25°C)
Amber 190/195	91	196	4.0
Steam Stripped 170/175	80	176	8.5
Cerese Yellow	77	171	12.5
"Superla Light Yellow"	79	174	11.5
"Petrosen A" (Yellow)	75	167	19.0
"Be Square White"	78	172	21.5
Amber 185/190	88	190	20.0
"Petrowax"	76	169	33.5
Amber 170/175	80	176	17.0
"Sun 12-90"	81	177	10.0
"Micropet"	73	163	99.0

Viscosity of Microcrystalline Waxes. Microcrystalline waxes of a plastic consistency have relatively high viscosities. A plastic wax of 142°F

melting point will have a viscosity of 31 centistokes at 75°C (167°F); one of 165°C melting point a viscosity as low as 18 centistokes. A paraffin wax of 132°F melting point will have a viscosity of only 5 centistokes at 75°C. The viscosity of low-melting microcrystalline waxes drops abruptly with an increase in temperature. For example, a wax of 142°F melting point having a viscosity of 46 centistokes at 46°C showed a drop in viscosity to 24 centistokes at 84°C. In the case of the crystalline paraffin waxes and the plastic microcrystalline waxes there is no pronounced rise in viscosity as the solidification point of the wax is approached from either the rising temperature or the falling temperature side, nor is there any indication of hysteresis for such waxes. In the case of the hard microcrystalline waxes there is a pronounced hysteresis in viscosity on the rising temperature side. (Cf. Marshall, A. W., *Anal. Chem.*, **22**, No. 6, 844 (1930).

Electrical Properties of Microcrystalline Waxes

Electrical tests on microcrystalline waxes have been expressed as radio frequency of 1 megacycle for the dielectric constant, power factor, and loss factor, tests at 60 cycles for dielectric strength, tests on direct current for volume resistivity, etc. At 20°C the dielectric constant values approximate 2.2 for 60, 10^3, and 10^6 cycles for microcrystalline waxes of 195°F melting point, and 2.4 at 60°C. Waxes of 185°F melting point have a dielectric constant of about 2.6 at 20°C, and 2.5 at 60°C. Power factor is expressed as such, or as a percentage. At 60 cycles the power factor for a 195°F melting point wax was given as 0.0022 or 0.22 per cent at 60 cycles at 40°C, and the loss factor (2.2×0.0022) as 0.0088. The potential breakdown (v/mil) ranges from about 1500–2100 for the higher melting point waxes at 20°C, but is only half the amount at 40°C. Volume resistivity ranges from about 3 to 7×10^{15} ohms-cm at 20°C at a relative humidity of 60 per cent, for higher melting point microcrystalline waxes. This is the equivalent of 3 to 7 hundred million megohms-cm. The dielectric strength at 25°C of one brand of wax is given as 430 volts/mil at a 50-mil gap.

Solubility of Microcrystalline Waxes in Solvents

Generally speaking, microcrystalline waxes have a low order of solubility in polar solvents, and are soluble to an appreciable extent in nonpolar solvents at ordinary room temperature, and extremely soluble at advanced temperatures (e.g. 150°F). They are ordinarily rated as insoluble in methanol, ethanol, isopropanol, butanols, and amyl alcohol at room temperature; likewise in isopropyl acetate, ethylene dichloride, nitrobenzene, furfural, phenol, cellosolve, and "Chlorex." They are soluble in chloroform, carbon tetrachloride, benzene, toluene, xylene, and turpentine; and slightly soluble in VM&P naphtha, Stoddard solvent, and kerosene.

The higher-melting microcrystalline waxes (e.g., 190/195) are less soluble in solvents than the lower-melting waxes (e.g., 170/175). For example, the former has a solubility of 0.6 gram per 100 ml of ethylene dichloride, whereas the latter has a solubility of 4.5 grams in the same solvent, both at 150°F temperature. Cloud points (indicating the degree of solubility) of both the 170/175 and 190/195 grades of waxes in various solvents in ratios of 1, 5, and 10 grams of wax in 100 ml of solvent, have been listed by the Wax Division of the Bareco Oil Company, and are given in Tables 67 and 68.

TABLE 67. CLOUD POINTS OF MICROCRYSTALLINE WAX

Solvent Used	Cloud Point °F		
	1 g wax	5 g wax	10 g wax
Normal butyl alcohol	173	196	198
Secondary butyl alcohol	136	150	155
Normal propyl alcohol	158	174	178
Isopropyl acetate	143	154	155
Chloroform	94	108	114
Ethylene dichloride	128	142	144
Benzene	99	114	118
Toluene	94	109	116
Xylene	98	112	120
Nitrobenzene	147	165	170
Turpentine	92	134	140
VM&P naphtha	105	114	122
Stoddard solvent	116	134	145
Kerosene	100	140	132
"Chlorex"	174	5g insol. at b. pt.—	
Carbon tetrachloride	90	104	108

TABLE 68. CLOUD POINTS OF MICROCRYSTALLINE WAX 190/195

Solvent Used	Cloud Point °F		
	1 g wax	5 g wax	10 g wax
Normal butyl alcohol	190	203	205
Secondary butyl alcohol	154	167	171
Normal amyl alcohol	176	192	194
Isopropyl acetate	164	175	176
Chloroform	103	126	138
Ethylene dichloride	151	158	160
Benzene	114	130	135
Toluene	110	128	134
Xylene	112	132	136
Nitrobenzene	116	180	184
VM&P naphtha	120	131	138
Stoddard solvent	100	122	152
Kerosene	122	140	145
"Chlorex"	174	5 g insol. at b. pt.	
Carbon tetrachloride	102	120	125

Pennsylvania "Micro Wax"

A microcrystalline wax prepared by the Quaker State Oil Refining Corporation from Pennsylvania crude oil is a very tough, flexible, dry, and substantially oil-free wax of high tensile strength. Because of the difference in its crystalline structure as compared with regular paraffin waxes, it will bend and can be flexed while cool, without the crumbling or breaking away experienced when handling ordinary crystalline waxes.

"*Micro Wax*" has a melting point of 63.3°C (146°F), a viscosity of 82–83 at 99°C (210°F), a needle penetration of 22 at 25°C (77°F) by the ASTM method; it has excellent electrical insulation qualities, and strong adhesive characteristics. It is marketed in colors from white to amber. "Micro Wax" has very high oil absorptive qualities.

The following constants for "Micro Wax" are those listed by the refiner at Bradford, Pennsylvania.

Matter insoluble in benzene	0.1% max.
Saponification number	0.05–0.10
Corrosive properties	
(a) Reaction to litmus	Neutral
(b) Reaction to copper	None
Melting point—ASTM D 127–30	145–146°F
Flash point—Cleveland Open Cup	500–525°F
Fire test	580–595°F
Viscosity—SUS @ 210°F	75–85
Needle penetration—ASTM D 5-25	20–23
Specific gravity at 34°F—solid	0.890–0.900
Tensile strength—Perkins Tester	220 psi
Refractive index—Sodium D line—80°C	1.4450–1.4460
Tackiness value—Bell Tel. method	0.50–0.60

Black Wax

Black wax is the name given to a "wax polymer" product obtained by blowing petrolatum or waxes derived from petrolatum with air. The process requires controlled oxidation of wax-containing petroleum fractions, involving control of time, temperature, pressure, and volume of air. The finished product has a tremendously increased viscosity, a shining black color although the charging stock may be green, a somewhat increased melting point, and a very low acidity (0.1 mg KOH by ASTM test for neutralization value).

In the process of David[8] the charging stock is placed in a confined shell still, which has perforated pipes in the nature of a "steam spider" in the bottom of the still. Air under pressure is introduced through piping having an orifice meter interposed. The evolved gases are run off at the top through a line to a condenser and separated for by-product recovery. The charge is heated to about 450°F before the air blowing begins, the reaction being exothermic enough to maintain the temperature without further heating. The air is blown through the mass for about 48 hours. The viscosity rises rapidly after the first 24 hours of blowing. About 4000 to 5500 cubic feet of air per hour were used by David to obtain 3,659 gallons of *black wax* from 4000 gallons of petrolatum. The black wax thus prepared had a melting point of 129°F, an open cup flash of 465°F, and a viscosity of 401 at 210°F Saybolt Universal contrasted with 101 for the charge. Black wax is suited for waterproofing and insulating.

Determination of Oil Content in Microcrystalline Waxes

The oil content of a microcrystalline wax is determined by freezing out the wax at a very low temperature from either a solution of the specimen tested in (a) methyl ethyl ketone, or (b) ethylene dichloride and then evaporating off the solvent. The oil from MEK, however, includes some of the relatively high molecular weight forked-chain hydrocarbons of very low freezing point, which may constitute about half of the oil. The oil obtained by the ethylene dichloride is generally speaking a true oil, that is, of a lower molecular weight and lower freezing point than the original wax specimen.

Paraffin—Microcrystalline Wax Blends

When a microcrystalline wax is added to melted paraffine it acts like a solute with paraffine the solvent, the melting point of the blend is greatly elevated, and the crystallization of the paraffine is depressed. The behavior is that of a two-phase system until about 15 per cent of the microcrystalline wax has been added. After that the paraffin wax begins to lose its identity, and this is first manifested by furrows on the surface of the congealed melt. When the microcrystalline wax, in this instance petrolatum wax, is 30 per cent of the whole the furrows begin to disappear entirely. With the addition of 15 per cent of the petrolatum wax the melting point of the paraffine is elevated from 130 to 160°F (see tabulation below). Were there only a single-phase system the actual rise would be from 130 to 139°F, based upon a straight-line curve plotted with melting point

against the percentage of one of the components

% Petrolatum Wax 180/190	% Paraffin Wax 128/130	M. P. (ASTM) (°F)
0	100	130
1	99	131
2	98	133
3	97	136.5
5	95	144
10	90	153
15	85	160
20	80	163.5
30	70	168
40	60	173.5
50	50	177
65	35	180
80	20	182.5
90	10	184
100	0	188

Uses of Microcrystalline Waxes

Out of a total production of 1,347,920,000 pounds of petroleum waxes in the United States in 1951, it has been estimated over 225,000,000 pounds were microcrystalline waxes. Many uses of these waxes are listed below:

Adhesives for laminating
Artificial fruits and flowers
Barrel lining
Beater size for various paper stocks
Belting impregnation
Beer can lining
Binding agents
Blasting supplies
Bottle cap liner coatings
Brewers' pitch composition
Candles
Capsules
Carbon papers
Cheese coatings
Chewing gum ingredient
Collapsible tube lining
Cosmetic creams
Crayons
Dehydrated food packages
Deicing compound
Dental waxes
Dressings for mechanical belts
Drinking cups
Egg preservatives
Electrical insulation
Field ration packages
Heat sealing compounds
Histological mounting wax
Horticultural wax
Laminants for paper, etc.
Lining for acid pipelines
Lipsticks
Meat coatings
Metal drum lining
Mildewproofing
Ointments
Ordnance packing
Paperboard cartons and drums
Paper milk bottles
Polishes
Printing inks ingredient
Radio parts
Rain clothing
Rubber compositions
Rust preventatives
Sealing and luting compounds
Ship launching grease
Shoe and leather treatments
Soda straws
Sound records
Stop-off for glass etching
Tank car treatment for wine, etc.

Floor wax	Typewriter ribbon
Food wrappers	Vegetable coatings
Fruit coating	Wax acid bottles
Galvanized iron wire coating	Wax emulsions and sizings
Glass fabric impregnation	Wax figures and toys
Grease and waterproof coatings	Yarn lubricant for wool, etc.

Preventing Oxidation of Wax Melts and Effect of Metals

The prevention of oxidation of petroleum waxes when their melts are subjected to continuous heating must be considered in connection with specific uses. The hydrocarbons will oxidize and decompose sufficiently to yield measurable amounts of acids and esters; aldehydes and ketones are formed to a lesser degree, unless precaution is taken in handling the melts. Both surface and autoxidation can take place under conditions of industrial use[44]. Decomposition is usually accompanied by the development of a slight acroleinic or burnt odor, a similar taste, and darkening of the color to a slight degree where the wax is chilled. If the temperature of the melt is maintained at 10°C (18°F), or less, above the melting point of the wax, the oxidation is slight even over a duration of days of heating, provided the wax is being heated in a suitable vessel. At a temperature of 40°C (72°F) above the melting point of a hydrocarbon wax, sufficient decomposition may set in during 24 hours in a glass vessel to yield traces of fatty acids, and a slightly reduced melting point. In 72 hours a titratable amount of fatty acid is evolved, and after a week's period the neutralization and saponification numbers will be definite fractions of 1 per cent. There is less oxidation with a petroleum ceresin, or microcrystalline wax of low oil content, than with a paraffin or ordinary petrolatum wax, under similar conditions of heating. The oxidation of paraffin waxes and the like is measured by peroxide number.

Concomitantly with the oxidation which takes place there is a lowering of the melting point which may approach 1°F in one day's heating of a microcrystalline wax at 250°F in a nonmetallic vessel. Oxidation takes place more readily in vessels made of brass, copper, zinc, and monel metal, and thus these metals should not be used for holding or contacting melted waxes. A petroleum ceresin heated at 250°F continuously over a period of 14 days in a copper vessel gave a saponification number of 0.75, contrasted with about one-third that amount when a glass vessel was used. Aluminum is a desirable metal for a wax kettle as is also stainless steel. For pour pans and molds, iron, aluminum, or tinned steel are generally used. A wax which has been treated with silica gel is quite stable to oxidation. Surface oxidation as well as autoxidation can be prevented by bubbling small quantities of CO_2 gas through the melt.

The effect of different conditions of exposure on the oxidation of "S/V

TABLE 69. EFFECT OF TEMPERATURE AND METAL ON OXIDATION OF "S/V PETROSENE A"

(Determinations made by Socony-Vacuum Oil Co.)

	Color ASTM	Color Lovibond	Acid Value	Sapon. No.
Original wax	Lt 2	5	0.00	0.00
Effect of temp.*				
200°F	2	5.5	0.00	0.00
250°F	Dk 2½	8	0.05	0.30
Effect of metal†				
Iron	Dk 3	8	0.06	0.74
Stainless steel	Lt 3½	14	0.03	0.56
Aluminum	Lt 4½	25	0.03	1.80
Brass	Lt 6	85	1.1	1.9
Copper	Dk 8	175	1.2	3.1

* Heated in glass for 24 hr.
† Heated at 250°F for 24 hr.

Petrosene A" given in Table 69 illustrates the oxidation characteristics of the microcrystalline waxes.

Antioxidants for Waxes

Paraffin wax, microcrystalline wax or a modified wax blend when in use for coating or lining containers, etc., is often subjected to hours of holding temperature of the order of 160 to 210°F, whereby the wax undergoes partial oxidation. According to Seubert and Andrews[44], some of the effects of oxidation observable in the resolidified wax are loss of hardness and tensile strength, discoloration, and offensive odor. Antioxidants, also called inhibitors or stabilizers, are occasionally added to waxes for the purpose of stabilizing them. The antioxidants include β-oxyanthraquinone ditolylamine, di-*tert*-butyl *para*-cresol (DBPC), gum benzoin, benzoic acid (sublimes at 100°C), gum guaiac, citric acid, high molecular weight alcohols, and long-chain hydrocarbons such as F-T Wax 300. One of the more effective modern stabilizers is DBPC manufactured by the Koppers Company, Pittsburgh, Pa. "Ionol" of the Shell Corporation, chemically speaking is 2,6-di-*tert*-butyl 4-methyl phenol and is an efficient stabilizer. Like DBPC it is of a low order of toxicity. "Ionol" is a pale yellow to colorless crystalline product, stable to light and heat, and melts at 70°C.

A batch of fully refined paraffin wax of high melting point usually requires the addition of only 0.004 to 0.05 per cent of the modern stabilizers. There are occasions where 0.1 to 0.2 per cent of the inhibitor may be required to stabilize the wax when operating at high temperatures[44]. A paraffin wax (138/140°F-AMP) which was aerated with air at 220°F developed a peroxide number of 3 in 24 hours, and of 28 in 48 hours. With the addition of a minimum amount of stabilizer the peroxide number could

be maintained at 0. The stabilizer protects the color and improves the odor of paraffin wax. The efficiency of a stabilizer is analytically determined by ascertaining the peroxide number, employing at the start a minimum amount of inhibitor at a prescribed temperature over a given period of time, always using a specimen of untreated wax as a control.

Antioxidants or stabilizers of the "Ionol" type are recommended as additives when preparing emulsions of rubber latices, in which case the chemical is melted together with the wax, such as microcrystalline wax, and the emulsifying agents (e.g., "Span" and "Tween") are added to the molten wax. The latex in water is slowly added and efficiently stirred in the mixture. As the addition of water is continued the resulting emulsion forms a stable fine-particle size dispersion of the rubber, and the wax functions as a crystal growth inhibitor.

References

1. Adams, E. W., and MacLaren, F. H. (Standard Oil of Indiana), U. S. Patent 2,127,668 (1938).
2. Anonymous, *J. Inst. Petroleum* **29**, 361–363 (1943).
3. Anonymous, *Lubrication*, **32**, No. 12, 133–140 (1946).
4. Bell, H. S., "American Petroleum Refining," 2d. Ed., p. 362, New York, D. Van Nostrand, Co., Inc., 1930.
5. Buchler, C. C., and Graves, G. D., *Ind. Eng. Chem.* **19**, 718 (1927).
6. Carpenter, J. A., *J. Inst. Petroleum Technol.*, **12**, 288–315 (1926).
7. Clary, B. H. (Bareco Oil Co.), paper entitled "A Discussion of Petroleum Waxes," CSMA Meeting Dec. 8, 1952.
8. David, A. D., U. S. Patent 2,100,070 (1937).
9. Diggs, S. H., Beard, R. E., and Page, Jr., J. M., U. S. Patent 2,050,428 (1936).
10. ———, and Buchler, C. C., *Ind. Eng. Chem.*, **19**, 125 (1937).
11. Dons, E. M., and Mauro, O. G., U. S. Patents 2,301,965, 2,302,428, 2,302,432, 2,302,433 (1942).
12. Dover, M. V., and Helmers, C. J., *Ind. Eng. Chem.*, **27**, 455–458 (1935).
13. "Encyclopedia of Chemical Technology," edited by Kirk and Othmer, New York, Interscience Publishers, Inc., 1951.
14. Ferris, S. W., and Cowles, H. C., *Ind. Eng. Chem.*, **37**, 1055 (1945).
15. Francis, F., *et al.*, *J. Chem. Soc.*, **121**, 1529, 2804 (1922).
16. Galle, E., *et al.*, *Öle, Fette, Wachse*, **1935**, No. 1, 17; No. 2, 10–12.
17. Giller, E. B., and Drickamer, H. G., *Ind. Eng. Chem.*, **41**, 2067–2089 (1949).
18. Govers, K. (Indian Refining Co.), U. S. Patent 2,067,050 (1936).
19. Gross, H. H., and Overbaugh, W. V. (Texas Development Co.), Canadian Patent 350,567 (1936).
20. Henderson, L. M., Ferris, S. W., and Cowles Jr., H. C., U. S. Patent 1,937,518 (1933).
21. Jones, L. D., and Blachly, F. E., *Ind. Eng. Chem.*, **21**, 318 (1929).
22. Jones, L. D. (Sharpless Specialty Co.), U. S. Patent 2,067,193 (1937).
23. Knowles, C. (Texas Co.), U. S. Patents 2,054,429 and 2,054,430 (1936).
24. Krafft, F., *Ber.*, **19**, 2223 (1886), *ibid.*, **29**, 1323 (1896), *ibid.*, **40**, 4779–4784 (1907).
25. Mabery, C. F., *Proc. Am. Acad. Arts Sci.*, **37**, 565 (1902); *Am. Chem. J.*, **33**, (1905).
26. Manley, R. E. (Texas Co.), U. S. Patents 2,054,429 and 2,054,430 (1936).

27. ———, U. S. Patents 2,067,128 and 2,067,196 (1936).
28. Marcusson, J., *Chem. Ztg.*, 39, 581–582, 613–616 (1915).
29. Mazee, W. M. (Batavian Petroleum Co., Amsterdam), *Rec. trav. chim.*, 67, 197–213 (1948) (in English).
30. Metayer, L., German Patent 257,471 (1911).
31. Minchin, S. T., *J. Inst. Petroleum*, 34, 542–587 (1948).
32. Myers, L. D., and Stegeman, G., *Ind. Eng. Chem.*, 20, 638 (1928).
33. Nenitzescu, C. D., and Irimescu, I., *Österr. Chem. Ztg.*, 44, 1–4 (1941).
34. Padgett, F. W., *et al.*, *Ind. Eng. Chem.*, 18, 832–835 (1926).
35. Page, Jr., J. M., *Ind. Eng. Chem.*, 28, 7 (1936).
36. "Pharmacopoeia of the United States of America," XI, p. 276, Printed by Mack Printing Co., Easton, Pennsylvania, Agent, 1936.
37. Poell, H., Technical Univ., Vienna, Third World Petroleum Congress, The Hague, The Netherlands, May 28–June 6, 1951; *cf. Chem. & Eng.*, 58, No. 11, 348 (1951).
38. Rau, K., U. S. Patent 2,188,795 (1940).
39. Reistle, C. E., and Blade, O. C., "Paraffin and Congealing Oil Problems," *U. S. Bur. Mines Bull. 348* (1932).
40. Rhodes, F. H., *et al.*, *Ind. Eng. Chem.*, 19, 935 (1927).
41. Sachanen, A. N., "The Chemical Constituents of Petroleum," p. 286, New York, Reinhold Publishing Corp., 1945.
42. Sakhanov, A. N., *et al.*, *Nat'l. Petroleum News*, 23, No. 16, 49; No. 17, 67; No. 18, 51; No. 19, 71 (1931).
43. Sawyer, M. F., *et al.*, *J. Inst. Petroleum*, 27, No. 208, 1–14 (1941).
44. Seubert, R. F., and Andrews, E. D., *Modern Packaging*, 26, No. 4, 153–154 (1952).
45. Taub, H., and Zweig, S., *J. Am. Pharm. Assoc.*, 28, 135–139 (1939).
46. Tears, C. F. (Warren, Pa.), U. S. Patent Reissue 20,623 (1938).
47. "Tonsil," brochure of Vereinigte Bleicherde Fabriken A. G., Munich (undated), distributed by U. S. and Canada selling agents, L. A. Salomon, New York.
48. Warth, A. H., and Bulatkin, I., unpublished reports.
49. Weingaertner, A., U. S. Patent 365,355 (1906).
50. Wilson, R. E., and Wilkin, R. E., *Ind. Eng. Chem.*, 16, 9–12 (1924).

6. Synthetic Waxes

Most of the synthetic waxes are waxes only in the sense that they possess physical properties akin to the natural waxes. The production of synthetic waxes has been steadily increasing from year to year. Statistically, the chlorinated paraffines are not generally included in the production and sales volume of synthetic waxes, since they are regarded as simply modified paraffin waxes. For convenience they will be included here with the synthetic waxes. About 25 million pounds of synthetic waxes were produced in the United States in 1951, valued at $8,000,000. Of the chlorinated paraffines somewhat over 24 million pounds are produced annually, with a sales volume approaching $3,000,000. The average price for a synthetic wax is in the range of 26–40 cents per pound, in contrast to the average price for a chlorinated paraffine of only 12 cents per pound.

Classification of Synthetic Waxes

The synthetic waxes may be divided into groups as follows:

(1) Long-chain polymers of ethylene with OH or other stop length grouping at end of chain. An example is "A-C Polyethylene #6."

(2) Long-chain polymers of ethylene oxide combined with a dihydric alcohol, namely polyoxyethylene glycol. An example is "Carbowax 4000."

(3) Halogenated hydrocarbons, either straight-chain or cyclic. Examples are the chlorinated paraffin waxes, and the chloroparaffin cyclic condensation waxes or directly chlorinated naphthalenes, as the "Halowaxes."

(4) Montan wax derivatives of very high molecular weight. Waxes of very high molecular weight are prepared by heating montan wax (a high molecular weight ester wax) with a catalytic agent to remove carboxyl (CO_2) groups, so as to form very long-chain hydrocarbons and alcohols; the decarboxylated product which contains unsaturated constituents is then directly hydrogenated to obtain the end product, such as "I.G. Wax Z." Or the deresinified natural wax (i.e., montan wax) is oxidized with chromic acid to produce an emulsifiable wax, such as "Gersthofen Wax S," which can be reacted upon with polyhydric alcohols in different ways to produce highly emulsifiable waxes as "Gersthofen Wax OP" and several others.

(5) Alkyl esters and polyhydric alcohol (polyol) esters of hydroxy acids.

Examples are the C_{10} to C_{18} alkyl esters, and the ethylene glycol monoester of 12-hydroxystearic acid.

Waxy polyol ether-esters, for example, polyoxyethylene sorbitol. Polyol-ether-ester derivatives of natural waxes, such as beeswax and woolwax.

(6) Synthetic hydrocarbon waxes prepared by the water-gas synthesis in which carbon monoxide (CO) is reduced by hydrogen (H_2) under pressure by means of a catalytic agent. For example, *contact waxes* made by a modification of the Fischer-Tropsch synthesis; and the Fischer-Tropsch waxes "F-T 200" and "F-T 300."

(7) Hydrogenated Waxes. (a) Waxlike products prepared by fully hydrogenating drying and semidrying oils; for example, "Coto flakes" from cottonseed oil, a semidrying oil. (b) Wax product prepared by fully hydrogenating castor oil (trihydroxy stearin); for example, "Castorwax." (c) Waxes prepared by optimum hydrogenation of oils under excessive temperature and pressure conditions to produce higher alcohols.

(8) Waxlike ketones, straight-chain and cyclic. (a) Symmetrical ketones produced by the catalytic treatment of the higher fatty acids; for example, *laurone*, *palmitone*, and *stearone*. (b) Unsymmetrical ketones produced by the Friedel-Crafts' condensation of fatty acids and the like with cyclic hydrocarbons; for example, waxlike end products such as *furyl heptadecyl ketone* and *phenoxyphenyl heptadecyl ketone*.

(9) Wax esters, of the natural wax type, prepared by heating fatty alcohols with fatty acids, or halogen derivatives of fatty acids, while passing a stream of CO_2 gas through the molten mixture. An example is synthetic *cetyl stearate*.

(10) Amide derivatives of fatty acids. The amides of fatty acids of 12 to 18 or more carbons are waxlike. They are prepared by reacting the fatty acid with dry ammonia under pressure. Examples are the commercial products known as "Armid HT" and "Armid C."

The length of the chain may be increased by heating fatty acids with an amino alcohol ($H_2N \cdot CH_2(CH_2)_x \cdot CH_2OH$), or by coupling two mols of amide with formaldehyde by means of an acid catalyst to form a methylene *bis*amide, as exemplified by the waxlike product known as "Armowax."

Waxlike products are produced likewise by employing with formaldehyde a strongly basic secondary amine (e.g., product of Resinous Products & Chemical Company). Hydroxy fatty acid (ω-$C_{10}H_{20}O_3$) when reacted with a long-chain amine (C_{18} and/or C_{16}) produces a hard wax of high melting point (e.g., product of American Cyanamid Company)[12].

Phenyl amidation of a straight-chain acid of 10 or more carbons to produce an anilide, for example, *stearanilide*.

(11) Imide (*N*) condensation products that are waxlike are those of the condensation reaction of a higher fatty acid with phthalic anhydride and

an aliphatic amine to produce phthalimides. An example is *N-octadecyl phthalimide* which is of notable commercial value.

An amide with straight-chain hydrocarbon groups is prepared by ketonizing fatty acids from fish oils, and the hydrogenating of ketones to produce the end product, e.g., so-called *synthetic ozocerite*.

(12) Reaction products of a monoethenoid hydrocarbon and a silicon halide. For example, with ethylene and silicon chloride as the reactants, a greasy to waxlike polmer of 85–110°C melting point is obtained, namely "Scott's silcon" product useful for self-polishing waxes.

(13) Polyoxyethylene fatty acid esters, for example, polyethylene glycol monostearate, and polyethylene hexitol monostearate.

Derivatives of polyoxyethylene sorbitol and the free acid component of a natural wax, such as beeswax or lanolin, for use in cosmetics.

(14) Miscellaneous synthetic waxes—unclassified. For emulsifiable synthetic waxes in general, see Chapter 8.

(I) LONG-CHAIN POLYMERS OF ETHYLENE

Polyethylene

Polyethylene is produced by the polymerization of ethylene, a gas primarily obtained from petroleum. The basic structure, $(CH_2—CH_2—)_n$, is not far different from that of a high molecular weight paraffin of petroleum origin. The process of producing polyethylene waxlike material will be referred to later. A typical polyethylene has a sequence of many side-chain methyl groups and a lesser number of methylene groups in the molecule. A polyethylene molecule in addition to the short-chain branches has a small number of longer branches; the average number of branch points increases with increasing molecular weight.

Polyethylenes which have a molecular weight of less than 6000 have waxlike characteristics. Polymers of 2000–4000 are definitely waxes. The relative degree of short-chain and long-chain branching of a sample, rather than the exact molecular weight, will influence the viscosity, crystallinity, toughness, and other physical characteristics of these waxlike polymers.

Linear polymers which have a molecular weight of above 12,000 are classed as "superpolymers," and are definitely resins; those ranging between 4000 and 12,000 in molecular weight are wax-resins. The resins with a molecular weight of 14,000 or less change from a solid to soft plastic mass when subjected to a temperature of 107–109°C (225–235°F). The low molecular weight solid grades (e.g., mol. wt. 2100 or thereabouts) produce fluid melts in the range of 97–106°C (207–233°F), and are more readily dispersed in waxes than the wax-resins. When admixed with paraffin wax they yield lower viscosities and lower cloud points, an advantage in paper coating work, etc.

Manufacture of Polyethylene. Polyethylene is prepared from purified ethylene gas in a suitable reaction vessel with the aid of a catalyst under conditions of combined high temperature and high pressure. The end product is removed from the reactor in some processes as it is formed. In one method the stainless steel reaction vessel is filled with oxygen-free nitrogen and some anhydrous benzene to which has been added a very small amount of a benzene solution of an organic polyperoxide. Organic polyperoxides are compounds containing two or more peroxy linkages. A polyperoxide from acetone and methyl ethyl ketone is prepared by adding to this solvent mixture an extremely cold (−18°C) mixture of sulfuric acid (70%) and hydrogen peroxide (H_2O_2). After dilution with water the resultant polyperoxide is separated as an upper layer, washed, and purified. These polyperoxides are also suited to polymerize other alkenes, vinyl compounds, etc. In preparing polyethylene the nitrogen in the reactor is removed and ethylene added to a pressure of 165 atmospheres and heated to 125°C, where the ethylene pressure is raised to 500–600 atmospheres and the polymerization allowed to proceed with agitation for 18 hours, maintaining the pressure by the addition of more ethylene. At the end of this time the excess of ethylene is bled off and a white solid C_2H_4 polymer of 13,400 molecular weight or thereabouts is obtained [E. I. du Pont de Nemours & Company, Inc., British Patent 604,580 (1948)]. The C_2H_4 polymers are useful for hot-dipped and melt-spray application, for conversion to wrapping foils, films, fibers, etc. Polyethylene is also formed by polymerization of ethylene in a continuous process at pressures of 1000–2000 atmospheres in a coil reactor at 168–199°C.

Erchak[23] describes a high-melting polyethylene wax (melting in the range of 82–100°C) of the formula:

$$Me(C_2H_4)_nC(OH)Me_2$$

prepared by polymerizing $CH_2 = CH_2$, preferably of 99 plus per cent purity, containing 1.1 to 2 per cent hydrogen peroxide and an amount of isopropyl alcohol, Me_2CHOH corresponding to 5–10 per cent of the volume of the reaction zone. The reaction is carried out in a reactor under prescribed conditions of heat and pressure. The n in the formula given above is possibly of the order of "140" for a grade of polyethylene of wax-like properties and which has a molecular weight slightly in excess of 2000.

Ethylene Interpolymer Waxes. Buckley and Ray[14] prepared waxes having improved dye compatibility by copolmerizing ethylene (C_2H_4) and allyl or methallyl alcohol at 60–200°C under pressure with a free-radical catalyst, such as an organic peroxide or an azo-nitrile. The wax can be made with an OH content up to 5 per cent but 1½ to 2½ per cent is preferred. For example, 5 parts of allyl alcohol and 0.8 part of azodiisobutyr-

onitrile are treated with 25 parts of C_2H_4 at 200 atmospheres and 80°C for 18 hours with stirring. The vessel is cooled, and the contents extracted with ether to remove any unreacted alcohol. About 8 parts of wax is produced by the interpolymerization. The wax has a melting point of 100°C, a molecular weight of 1800, and an OH content of 2.5 per cent. A mixture of 90 parts of ethylene polymer wax, 10 parts of paraffine, 1 part of stearic acid, and 1 part nigrosine (dissolved in 250 parts of white spirit) gives a paste suitable for black shoe polish. Waxes suitable for wax crayons and carbon papers are claimed to be similarly prepared[14].

Ethylene Copolymers. In a British patent granted to Perrin *et al.* and Imperial Industries, Ltd.[53] in 1938, are described high molecular weight compounds prepared by subjecting ethylene (C_2H_4) in the presence of other alkenes and compounds having one or more double bonds, to a pressure of at least 500 atmospheres and a temperature of 100–400°C. Unsaturated hydrocarbons suitable to produce dimers or polymers include isobutylene, 2-pentene, styrene, stibene, etc. Small amounts of catalyst, such as oxygen or benzoyl peroxide, may be used, and gaseous diluents such as nitrogen may be present. Certain of the copolymer products may be extruded or otherwise formed into films, threads, tubes, rods, sheets, and tapes. The more waxlike ones may be used as ingredients in polishes, formed into emulsions, and when partially hydrolysed, may be used as emulsifying agents.

"A-C Polyethylene Waxes." The polymerization of ethylene to produce waxes or waxlike materials may be conducted in the presence of a modifier to obtain products of the formula:

$$A(C_2H_4)_nB$$

in which the composition of the terminal groups A and B is determined by the modifier used. A wax of this description is marketed by the Semet-Solvay Petrochemical Division, Allied Chemical & Dye Corporation, under the trade-mark "A-C Polyethylene." The molecular weight of the polyethylene wax is approximately 2000. Limited experimental quantities of a product known as "Alcowax" were produced for some time out of a pilot plant at Morristown, New Jersey, but a full-scale commercial production of a similar wax, under the name of "A-C Polyethylene #6" (and other numeral designations), is now in operation at the new Tonawanda refinery, Buffalo, New York. The latter uses the Lummus ethylene recovery system operating on bunker C oil, as the source of the polyethylene polymer waxes.

Physical Properties of Polyethylene Waxes. Polyethylenes of the waxlike type appear on the market in the form of pellets, flakes, or powder. They are hard, of white translucent color, tasteless, nontoxic, and

substantially odorless. They are resistant to water and chemicals. They are slightly soluble in turpentine, naphtha, xylene, and toluene, at room temperature, but insoluble in polar solvents—hot or cold. Polyethylene of about 2000 molecular weight will dissolve to the extent of 21 to 31 mg in 100 g of xylene at 180°F.

The melting point (ASTM D 87–42) of the polyethylene waxes ranges from 97 to 115°C depending on the reaction conditions taking place in the reactor in their making. Generally speaking, the melting points of polyethylene in the 2000 to 5000 mol range will range between 100.5 and 104°C.

The density ($d^{15.5}$) of polyethylene waxes is about 0.922. The durometer hardness approaches 100. The penetration value (100 g/5 sec/25°C) is 0.3–0.5 for wax of 5000 molecular weight, and 1.2–1.6 for wax of 2000 molecular weight. The needle penetration (mm in tenths) for the latter wax is 2.2 (30 sec/22°C) under a 200-g load. The tensile strength ranges from 1400 to 2600 psi, and elongation 200 to 800 per cent.

The absolute viscosity of 5000 mol weight polyethylene has been given as 152–154 cps at 300°F, and 100–108 cps at 350°F for "A-C Polyethylene #6," and 4000 cps at 284°F for #615 (5000 mol. wt.). The kinematic viscosity of a mixture of 10 per cent polyethylene (2000 mol. wt.) and 90 per cent paraffine (133/135 grade) is 9.5 centistokes, and with paraffine of 124/126 grade is 6.7 centistokes.

The addition of polyethylene wax to hydrocarbon waxes increases the melting points of such waxes to a marked degree. The cloud point of a 5 per cent mixture of "A-C Polyethylene G" (av. mol. wt. 2000) in paraffine has been given as 155°F. The information concerning the electrical constants of polyethylene is rather meagre. The dielectric constant, or specific induction capacity, is about 2.50 at 60×10^6 cycles; the volume resistivity (10^{13} ohms cm) is 1000; the dielectric strength (BV in volts per mil at 25°C) has been given at 2560 (mol. wt. not stated), and 1000–1100 (mol. wt. 21000). The power factor on latter material is given as 0.0003 (1000 c.p.s. at 25°C). The flash points range from 470 to 490°F.

The acid value of "A-C Polyethylene #6" is 0, saponification number 6–7, and iodine number 0.35.

"Epolene N Wax". "*Epolene N*" is a polyethylene wax produced by the Eastman Chemical Products, Inc., Kingsport, Tennessee. It has a molecular weight within the range of 2000–6000, a melting point of approximately 106°C, penetration hardness (mm in tenths, 100 g/5 sec/25°C) less than 1, acid and saponification numbers both less than 0.1, Brookfield viscosity 1900–2000 cp at 250°F. The cloud point of 3 per cent "Epolene N" in paraffin wax (m. 132–133°F) is 163–164°F, and of 5 per cent "Epolene N" is 170–171°F. It is produced and shipped in the form of pellets. The color (liquid), Gardner scale, is 1.

"Epolene N" like other polyethylene waxes has many fields of possible application, when admixed with petroleum and other waxes with which it is compatible. These fields include all types of polishes, candles, carbon paper, crayons, electrical services, food packaging, matches, paper coatings, printing inks, hot melts, wire and cable insulation, rubber compounding, etc.

(2) LONG-CHAIN POLYMERS OF ETHYLENE OXIDE COMBINED WITH DIHYDRIC ALCOHOLS

"Carbowaxes"

The "Carbowax" compounds, which are solid polyethylene glycols, are water-soluble, nonvolatile, unctuous compounds. The solid polyethylene glycols have a molecular weight in the range of 1000 to 7000, and have the physical appearance of waxes. In melting point, flash point, specific gravity, viscosity, and aqueous solubilizing action all increase with increasing molecular weights. "Carbowax" is the trade name given to these compounds by the Carbide and Carbon Chemicals Company. The composition of "Carbowax" has been disclosed by McClelland and Bateman[41] as consisting of one or more of the higher polyethylene glycols. The commercial "Carbowax" compounds are all mixtures of several polymers, and are rated according to their mean molecular weights, which are not necessarily designated by the numbers they bear. "Carbowax" has the general formula $HOCH_2(CH_2OCH_2)_xCH_2OH$. These compounds dissolve in water to form transparent solutions and are soluble in many organic solvents, but dissolve in aliphatic hydrocarbons to only a slight extent.

The compatibility of "Carbowaxes" with waxes and resins is very limited, whether in solution or in the form of hot melts. "Carbowax" is supplied by the manufacturer in several grades from soft to hard.

"Carbowax" Compound	Freezing Point Range (°F)	Flash (0°F)	Water Solubility at 68°F (% by weight)
1000	98–104	450	70
1500	100–106	425–430	73
1540	100–115	450	70
4000	127–133	475	62
6000	140–146	475	50 (approx.)

Uses of "Carbowaxes." Among the applications which have been developed for "Carbowax" are nail polish, shoe polish, remover cream, mold lubricant for rubber, and viscous rayon. It can be used as a substitute ifor glycerol in toilet preparations. According to a report published under a fellowship at the Mellon Institute, "Carbowax" is comparatively nontoxic; in cost it is about twice as much as propylene glycol. "Carbowax 4000" is of special interest to manufacturers of water paints, calsomines, shoe dressings, and sizing materials. It can be used to advantage in water-soluble

crayons for artists, in marking textiles when mark must later be eliminated, in etching fluids, and wherever it is desirable to have an excellent surface tension depressant. "Carbowax 1500" offers possibilities as a plasticizer in casein, gelatine, and glue adhesives; in sizes, binding agents, textile and paper softeners, lubricants, and preservatives. It can be used as a scrubbing liquid for air purification, in the formulation of belt dressings, and for cosmetics, lotions, and hair preparations.

The addition of "Carbowax" to polyvinyl alcohol improves the ease of stripping films from metal surfaces. The aqueous solution being dry cast comprises 10 to 25 per cent polyvinyl alcohol and 0.01 to 0.10 per cent "Carbowax" by weight. The "Carbowax" employed for this purpose must be at least 4 per cent soluble in water at 25°C.

(3) HALOGENATED HYDROCARBON WAXES

Chlorinated Paraffin Wax

Chlorinated paraffin, or *chloroparaffin* as it is also called, is a chemical which in consistency may be liquid, semifluid, or solid, depending upon the type of paraffin chlorinated and the degree of chlorination. Each H atom of the terminal CH_3 groups of the paraffin as it is replaced by a Cl atom increases the chlorine content of the end product by 11 per cent by weight, a trifle more or less, so that the chloroproducts have 11, 22, 33, 44 per cent or even higher of chlorine. For industrial use white crude scale paraffin is customarily used in making chloroparaffins, and ordinarily two grades, one of 40 per cent Cl and one 70 per cent Cl, are produced.

Girelli and Siniramed[29] of the Experimental Station Fuels, Milan, Italy, studied the influence of temperature and flow rate of chlorine gas on the yield and properties of chlorination products of paraffin waxes. Paraffin of 48°C (118.4°F) melting point and 370 molecular weight was directly chlorinated at temperatures of 80°, 100°, and 120°C. A flat maximum absorption of Cl appears at 100°C and the color of the liquid chlorinated paraffin becomes darker with increasing temperature. The most economical condition was a flow rate of 28 l Cl/kg/wax/hr, at 80°C, giving a product which contained 33.7 per cent Cl. Other conditions gave products ranging from 8.6 to 47.5 per cent Cl, of a white to yellow-brown color, a density (d^{25}) of 0.900–1.280, and a viscosity of 11.5–3019 centistokes. A minimum freezing point of −17°C was reached at a Cl content of 39.8 per cent. The commercial demand is mostly for a chloroparaffin of not over 40 and not less than 30 per cent chlorine.

Chloroparaffin is prepared by one of two methods: (1) The classic Bolley method[11] in which the chlorine is passed through melted paraffin until the desired Cl content is reached, the method above referred to; hydrogen chloride is evolved as a byproduct. For example, *slop wax* can easily be chlorinated by the Bolley method. (2) The Böhringer process[4], patented in

1910, in which chlorine is conducted into a solution or suspension of the material, such as *white crude scale paraffin*, in carbon tetrachloride (CCl_4), until the resultant product contains at least 30 per cent chlorine. Chlorination can thus be carried out at a low temperature and pressure, using the actinic rays of the sun as an activating agent. Solid products, water-white in color, and transparent can be obtained when the CCl_4 is recovered, provided a paraffin wax of sufficiently high melting point is used.

Chlorinated products can be made from paraffin, mineral, montan, and vegetable waxes, in which energetic chlorination is effected wholly, or partially in the presence of catalysts. For example, *flax wax* can be chlorinated to 36.2 per cent chlorine content. The olefins can be chlorinated highly, to a Cl content of more than 70 per cent. Many useful NH_3, OH, and SO_2H derivatives can be prepared from the chloroparaffins.

Commercial chlorinated paraffin is a colorless to amber-colored viscous liquid. It is marketed in 55-gallon drums containing 525 pounds, and in tank cars. Because of its splendid fire-retardant, moldproofing, and water-repellent properties it has been extensively used for the proofing of tent canvas. The grade with a 40 per cent Cl content is used as an ingredient in textile flameproofing compositions. It is used as a decontaminant for the human skin when exposed to gases such as mustard gas. It is also used as an additive to lubricating oils to impart extreme pressure characteristics, i.e., for metal cutting, etc. Such extreme pressure lubricants are offered by the Lubricol Sales Corporation, Cleveland, Ohio. Chloroparaffin is miscible in all proportions with castor oil, and will act as a stabilizer and agent in bringing about compatibility with mineral oils in the field of lubrication; it has been termed a *solubilizer*.

Chloroparaffin is listed as a plasticizer for vinylite resins, nitrocellulose, polystyrene, methacrylates, coumarone-indene and other resins. Solutions of chlorinated paraffine in aromatic solvent, other than mineral spirit, can be advantageously fortified by the addition of some more highly chlorinated body such as chloropropane. Chloroparaffin has excellent dielectric properties.

The 70 per cent Cl grade is said to be a replacement for chlorinated naphthalene ("Halowax") in flameproof electric wire insulation. Foundry cores are sprayed with a 15 per cent solution of chlorinated paraffine in a petroleum hydrocarbon solvent to prevent pinholing, particularly of aluminum castings. The preferred Cl content is 40 to 80 per cent, such as is found in "Chlorowax."

"Chloropane Wax 130."

This is an octachloropropane of a waxy structure resembling paraffine in appearance. It is a tough white crystalline wax possessing a camphor-like odor. It is insoluble in water; soluble in alcohol, ether, and most chlorinated

solvents. Its manufacturer, the Hooker Electrochemical Company, has given it the empirical formula $C_3H_{0.15}Cl_{7.85}$ with a molecular weight of 311, constituting about 85 per cent octachloropropane, and 15 per cent heptachloropropane (1,1,1,2,2,3,3). It has a melting point range of 110 to 135°C, with last crystal point at 130 to 135°C; it boils at 210 to 270°C at 760 mm pressure. It is compatible as a plasticizer with resins such as polyvinyl chloride, vinylite, styrene, urea formaldehyde, Piccolyte, phenol formaldehyde and methacrylates, as well as with rubber and certain rubber substitutes. Among suggested uses are the following: plasticizer, dielectric wax, ingredient in pyrotechnic compositions, chemically resistant lubricant.

"Chlorowax."

"Chlorowax" is the brand name for a chlorinated resinous paraffin, made by the Diamond Alkali Company. It contains about 69.7 per cent of chlorine. The product as it appears on the market is a brittle, pulverized, white, water-insoluble resin and not a wax. "Chlorowax" melts at 90°C (ball and ring method) and has a specific gravity (d^{25}) of 1.64. It is soluble in hydrocarbons, ketones, esters, nitroparaffins, and chlorinated hydrocarbons. It decomposes at 135°C. "Chlorowax" is of value as a flame retardant for protective coatings. It is used in electric cable-coating compositions and in flameproofing textiles. A more highly chlorinated paraffine is that of the Hooker Electrochemical Company, which contains 76 to 78 per cent of chlorine. This is a pale-colored, brittle resin, softening at 100°C, and used in paints to help them withstand severe weather conditions.

Chloroparaffin in Cyclic Condensation Products

Chloroparaffins may be condensed with naphthalene by means of a catalytic reactor, or with naphthalene already chlorinated, to produce hard waxes that have fire-retardant, electrical, insulating, and chemical-resistant properties. (Also see Chloronaphthalene Waxes, p. 453). Of this description are the "*Halowaxes*" and "*Seekay Waxes*," which differ only in the manner in which the chlorination has been carried out, the type of catalyst employed, and the flexibility of the resultant product. These products are obtained by chlorinating paraffines and condensing them with a double ring aromatic hydrocarbon, such as naphthalene, in the presence of a catalytic agent, aluminum chloride ($AlCl_3$).

Similar condensation products are of value as pour-point depressants (see p. 646). In the process of Davis[17] the chlorine is bubbled through the molten paraffin wax, and when 12 to 14 per cent of Cl is absorbed, the product is condensed with naphthalene using $AlCl_3$ as a reactor, the free HCl being expelled in the heat reaction to produce the end product. In the

process of Reiff[48] the chlorinated paraffin is condensed with phenol in a similar manner. Frolich[27] has prepared a condensation product similar to "Halowax" by reacting chlorinated paraffin wax with naphthenic acid. To this mixture $AlCl_3$ is slowly added, and the temperature slowly raised to 300°F. The reaction takes 5 hours. The flask is cooled and the contents diluted with kerosene and then neutralized with water and alcohol to hydrolyze the catalyst. The wax is recovered by distilling the kerosene layer separated from the sludge layer.

Chloronaphthalene Waxes

In chlorinating naphthalene, the formation of isomeric mixtures of a waxy appearance was first observed in 1833 by Laurant and so described by him [*Ann. Chem.*, **II**, 52, 275]. It is again mentioned by Emil Fischer in 1878 [*Ber.* **II**, 736]. The waxy appearance of mixtures such as these is purely artificial, since the properties which characterize natural waxes are absent, as they are in many other so-called synthetic waxes.

The synthetic waxes derived from chloronaphthalene regained their significance shortly after the turn of the century and particularly during the first World War, after being in oblivion for many years. In the United States it was primarily J. W. Aylsworth who called attention to these substances and induced their industrial application through a series of patents, which were taken out around 1900.

Aylsworth[2] impregnated wood, woven fabric, wallpaper, etc. with a chlorinated product of naphthalene, which he described as of waxlike consistence, and covered by his patent of manufacture. In the Aylsworth process, chlorine from electrolytic alkali manufacture is dried and made to react upon naphthalene at 100–150°C under a pressure of 10–50 lb per sq in., forming HCl and a waxlike chlorinated derivative of naphthalene, containing about 68 per cent Cl. This derivative sublimes at about 315°C without decomposition, melts at 128°C or thereabout, has a specific gravity (d^{15}) of 1.850, and is soluble in chloroform, carbon tetrachloride, and naphtha.

In Germany, several concerns produced chloro-wax cyclic condensation products during the war years 1914–1918 in order to meet the growing demand for available protective wax coating materials. Waxes of this kind were brought on the market under the trade names of "Perna," etc., and used to impregnate inserts in gas masks. The application made use not only of their waxy characteristics, but also of their extraordinarily high resistance to corrosive chemicals, a property ascribed to the high replacement of hydrogen by chlorine in their chemical composition. At about this time, additional patents of great significance were granted. Amongst them was the patent to Aylsworth[3] on his invention of November 8, 1913, which described an electrical condenser formed of conducting plates separated by a

dielectric formed of solid chlorinated naphthalene mixed with "orthocresol resin."

In the decade to follow, these substances received acceptance in the electrical field not only in the United States but also in Europe, and improved methods were devised for their production together with modification of the end products with meltable substances, such as paraffin waxes, which made them less hazardous to health in their application in the industries.

Engelhardt[22] in 1933 was granted a United States patent for a process which he had developed in 1927 for the I.G. Farbenindustrie A.G., in which chlorine is continuously introduced into a molten reactive mass, maintained at 5–10°C above the melting point of the material in each stage of the chlorination. The chlorination is continued until at least three Cl atoms have entered the molecule, and a waxy product has been obtained. Another method of production is based upon the observation that by means of fractional distillation there can be separated certain isomeric mixtures which on melting draw threads and therefore show a property which many a natural wax possesses.

The density of a chloronaphthalene is a function of its chlorine content. The approximate relationship between the degree of chlorination and density ($d^{15.5}$) and an approximation of the melting point is given in the following table:

Number of Chlorine Atoms	% Chlorine Content	Density (optimum)	Melting Point (°C) (R & B flow point)
3	45.1	1.48	65
4	52.5	1.50	74
5	58.3	1.56	95
—	59	1.57	94 (setting pt.)
6	63.5	1.68	122
—	65	1.74	130
7	66.4	1.83	136
—	68	1.90	124 ?
8	69.4	2.05	88 (capillary)

The chemical and physical properties of the chloronaphthalenes (ostensibly those in the range of 3 to 7 chlorine atoms) have been described by Halls[33] as follows: Density ($d^{15.5}$) 1.500–1.700, melting range 65–130°C, and specific inductance capacity 4.4–5.5 according to grade. On oxidation HCl is not split off, but on rapid heating the additive $C_{10}H_8Cl_4$ decomposes into HCl and 1,4-$C_{10}H_6Cl_2$. Tests show that copper, mild steel, or these metals coupled do not affect the waxes at 120–125°C in a dry atmosphere, or at 40–50°C in a humid atmosphere, nor are the metals corroded; but in the presence of water at 120–125°C copper is tarnished and HCl (0.001%) is produced.

Dermatitis is said to result sometimes from halogenated naphthalenes and diphenyls, and to some extent with chlorinated paraffin waxes other than "Chlorowax."

"Nibren Waxes"

The Farben Fabriken Bayer, Leverkusen, Germany produces today waxlike materials manufactured more or less according to the Engelhardt process[22], with the exception of small changes and improvements necessitated by periodically increased demand. They are marketed under the general name "Nibren Waxes." These waxes are furnished in the convenient form of flakes or in powder. In their original state they are pure white, but they can be dyed to all hues by means of "Sudan" dyestuffs. The "Nibren" waxes are made with increasing chlorine content; the chlorine determines the properties of the end product, particularly the degree of setting. Of all the commercially available "Nibren" waxes, the No. D 88 with a chlorine content of 49–50 per cent has the lowest setting point (92–96°C) whereas "Nibren Wax D 130" with a 59 per cent chlorine content has the highest (130–134°C).

"Nibren" waxes are characterized by their low viscosity at a temperature only a little above the melting point; by the ease of penetration of jute, cotton, silk, paper and wood without injury to the fiber; by high dielectric constants (E) of 4.5–5.5; and small power loss factors of 1×10^{-4} to 1×10^{-3}. For transmission work, "Nibren" waxes of the lowest melting point and highest dielectric constant (K) value of 5–5.5 are being used. For the impregnation of automobile condensers, "Nibren" waxes of the highest melting point (130–134°C) are used (in Europe) because of the high temperature which surrounds the condenser.

"Nibren" waxes which are cut or mixed with rosin or artificial resins can cause injury to the skin to persons allergic to such mixtures. A protective skin cream should be used as prophylactic to make the handling of "Nibren" wax mixtures a safe hygienic procedure. The specific gravity varies with the degree of chlorination and is extremely high (1.5–1.7) contrasted to other waxes. They are of value in weighting impregnated materials such as wood, carpets, runners, etc. "Nibren" waxes have about half the shrinkage of paraffin wax, are not oxidizable, and are permanent in their resistance to aging. They are soluble in the usual organic solvents, and by means of special solvents and emulsifying agents can be dispersed in the form of emulsions, for use as fungicide spray material and the like.

"Nibren" waxes have flame-retardant properties; in burning they liberate gaseous hydrogen hydrochloride which serves to extinguish the flame. Therefore they are useful for impregnating the braiding of electrical cables and conduits used in fire-exposed rooms and in mines, since the fire cannot extend along the lines.

"Halowaxes"

"Halowaxes" are hard, tough, pale yellow synthetic waxes having a chemical odor, more or less chlorine-like, and possess peculiar chemical and physical characteristics. There are several grades: (1) a hard crystalline solid, white to pale yellow in color with a density ($d^{15.6}$) of 1.560; (2), a hard semiamorphous solid of pale yellow color with a density of 1.680; and (3), a tough amorphous solid in like color having a density of 1.780. The melting points range between 95 and 136°C (203–276°F), the boiling points between 550 and 700°F, and the flash points between 284 and 392°F. The waxes do not support combustion so there is no fire point. The acid number is about 0.1. The coefficients of linear expansion range between 0.0008 and 0.00005 respectively for the solid waxes.

The "Halowaxes" are high in dielectric strength and have an extraordinary specific inductive capacity (4.5–5.5). They are neutral and noncorrosive to metals, are very moisture repellent, and melt to a liquid of low viscosity. These properties make them of great value in the electrical industry.

The Halowax Product Division, Union Carbide and Carbon Corporation, have developed two new chloronaphthalene products, one of which has the highest chlorine content (69.4%) it is possible to incorporate in such compounds, namely a product which is essentially *octachloronaphthalene*. Its high Cl content gives it exceptional flame resistance, high heat stability, and extremely low volatility. When ground in a powder it can be employed as an inert fillter for compounding with polymers to impart such important characteristics as flame resistance and improved electrical properties. Although the nature of the material classes it as a resin and not as a wax it is sold under the name "Halowax 1051 X." It is light yellow in color, melts at 83.3–87.7°C (capillary tube), and has a density (d^{25}) 1.95–2.10, penetration (200 g, 25°C) 1–3, power factor (1000 c.p.s. 25°C) 0.0011, dielectric constant (1000 c.p.s., 25°C) 2.5, vapor pressure (mm Hg, 130°C) 0.01.

The second of the new products, "Halowax 1052 X," is essentially *heptachloronaphthalene*, and is waxlike. It has a high chlorine content (65 per cent) and is useful in the compounding of rubbers with various plastics. It is light yellow, melts at 111–118°C, sp. gr. (d^{25}) 1.89–1.95, penetration (200 g, 25°C) 10–15, power factor (1000 c.p.s. 25°C) 0.0011, dielectric constant (1000 c.p.s., 25°C) 3.7, vapor pressure (mm Hg, 25°C) 0.03.

"Halowaxes" are widely used to protect fibrous materials from fire hazard, particularly in the insulation of electrical wires. They are used in paper electrical condensers because of its good capacitor performance. It is important that the paper employed be of exceedingly low ash content or free from electrolyte. Chloronaphthalene is extensively used in battery separators.

"Halowax" is employed in compounding many types of liquid, paste, and emulsified polishes. It aids in the bleaching of other darker colored waxes. It is, however, not practicable for any purpose relating to food packaging except in extremely small quantities in a wax composition, since it emits an objectionable aromatic odor. Flexible protective coatings can be made with chloro-waxes blended with petrolatum waxes. "Halowax 1001" (m. 196°F) is used primarily as an impregnant for paper-tubular capacitators. The estimated sales of chloro-naphthalenes as waxes is reported to be about 7 million pounds per year, valued at $2,250,000.

"Seekay Waxes"

The "Seekay" waxes are chlorinated naphthalenes manufactured by the Imperial Chemical Industries, Ltd., in England. They resemble natural waxes in appearance and also in their water-resisting properties, inertness to chemicals, and good insulation properties. In addition they have two important advantages: (a) they are nonflammable, and (b) they can be obtained with a melting point as high as 125°C. The waxes have definite fungicidal and insecticidal properties.

In color the "Seekay" waxes varies from dark brown or black-brown to pale yellow. Grades are available in melting points of 65–70°, 90–95°, 110–115°, and 120–125°C. The latter has a chlorine content of 65 per cent. "Seekay" waxes boil at 1 mm pressure at 143–190°C (290–375°F). The density of a "Seekay" wax (57–58% Cl content) is 1.550 at 15°C; specific heat 0.202 at 18°C, and 0.278 at 110–120°C; specific inductive capacity 5.4. The waxes have a slight odor. They are very soluble in dichloro- or trichloroethylene, benzene, ethyl ether, and acetone, but less soluble in amyl alcohol or methanol. They are compatible with bitumens.

"Seekay" waxes are useful for waterproofing, flameproofing, electrical insulation, insecticides, fungicides, and wax or bitumen blending.

Chlorinated naphthalenes must be handled with care and overheating should be avoided as the fumes or dust of these waxes are toxic to the skin.

"I.G. Waxes"

Historical. "I.G. Waxes" are as a whole an important group of long straight-chair synthetic products, which include hydrocarbons, alcohols, ketones, esters, and other derivatives, prepared from natural waxes, more particularly montan wax, as the basic raw material. Since the I.G. Farbenindustrie A.G. in Germany was dissolved at the end of World War II, a few of the "I.G. Waxes" have disappeared from the market altogether, as those made at Oppau (e.g., "I.G. Wax Z"), whereas others with the various "I.G." letter designations are again being made at Gersthofen under the name of

"Gersthofen Waxes" with identical letter designations. However, the "I.G. Waxes" will be described as such.

In 1940 Hamor[1] noted that "I.G. Waxes," which were capable of replacing carnauba wax in the production of leather polishes and creams, were made from purified montan wax, by esterifying or otherwise altering the COOH group of the high molecular weight aliphatic carboxylic acids comprising it. The *montanic acid*, exists very largely in a free condition, and can be esterified readily to an ester of a much longer carbon chain. This results in the production of a wax of very high melting point and other unique properties.

It was found by Jahrstorfer of the I.G. Farbenindustrie A.G. that the aliphatic acyl compounds of bleached montan wax could be linked together in an ester-like fashion by converting the carboxyl (COOH) groups of the free acids into other groups containing the —CO— linkage, which do not contain a carboxyl hydrogen atom, as for example ketones, anhydrides, and the like. This condensing-splitting action can be achieved by heating the wax under high pressure with a suitable catalyzer. Later Jahrstorfer found that it is frequently an advantage to subject the products either simultaneously or subsequently to a hydrogenating treatment.

In 1932 Pungs and Jahrstorfer[46] claimed that the properties of natural waxes can be improved by treatment with hydrogen at 100–150 atmospheres pressure and 200°C plus temperature in the presence of a cobalt or nickel catalyst. High molecular waxlike substances produced from high molecular compounds of oils and waxes containing a COOH group when treated catalytically so as to split off CO_2, and then hydrogenating the resultant product, will according to Jahrstorfer and Schwarte[57] provide substances good for dressing and impregnating all kinds of fiber, paper, etc. In splitting off the CO_2 group from the COOH containing wax, the powdered catalyst, such as nickel, iron, tungsten sulfide, or alumina, is spread on the carrier—like silica, silica gel, kieselguhr, or activated carbon—and mixed with the wax. The hydrogen treatment is conducted under high pressure in the presence of the catalyst at a temperature of 180–200°C.

In their U. S. Patent issued in 1938 the inventors[38] give several specifications for the preparation of "I.G. Waxes." In one example 1000 parts of brown montan wax is heated for 12 hours to 310°C while stirring with 200 parts of kieselguhr and 30 parts powdered iron. After filtering off the catalyst the wax has a melting point of 100°C which contrasts with 83°C for the montan wax. By catalytic hydrogenation of the product at 300 atmospheres and 250°C with a catalyst made by applying 20 parts of nickel to 8 parts of kieselguhr, a pure, colorless, hard product is obtained having the following characteristics: melting point 104°C, acid value 0, saponification number 0, hydroxyl value 2. This product is therefore practically a pure hy-

drocarbon of high melting point, identical to the product at one time marketed in America by the I.G. Farbenindustrie A.G., under the name of "I.G. Wax Z." It is interesting to note that the acid value (107) and the saponification number (143) of the montan wax are brought down to 0 in the production of "I.G. Wax Z."

The reactions may be postulated as follows. The ester, *montanyl montanate* (m. 89°C), of the deresinified montan wax when subjected to pyrolysis at low pressure is converted to montanic acid and the alkene $C_{28}H_{56}$ (*1-octacosylene*, m. 60°C).

$$C_{27}H_{55}COOC_{28}H_{57} \rightarrow C_{27}H_{54}COOH + CH_2{:}CH{\cdot}C_{26}H_{53}$$

At higher pressure, pyrolysis of the monoesters tends to form ketones. By catalytic hydrogenation, the reaction products, namely acid and alkene (1-octacosylene), can be converted to 1-octacosane, and by heat and pressure the *montanic acid* can be decarboxylated and the ketones reduced so that a high melting hydrocarbon wax is formed, which obviously consists of a mixture of hydrocarbons approaching $C_{55}H_{112}$ (m. 96°C) in composition, with slight amounts of ketones (m. 94–95.8°C) and resin of an extremely high melting point as impurities, giving in effect a wax product which approaches 100°C in melting point.

Gersthofen Wax Process and Equipment. The following is a description of the I.G. Wax process and equipment as it was in operation at the beginning of World War II. The procedures described are substantially the same as those followed by Werk Lech-Chemie Gersthofen (Farbewerke Hoechst A.-G.).

"The useful source of montan wax in Germany is the brown coal of 10–18 per cent wax content at Halle Riebeck where there is an extraction plant for raw wax. Finely pulverized brown coal is dried in a pipe drier with steam heat at 150–180°C to a moisture content of 10–12 per cent. The dried coal is then sieved to free it from dust, and extracted by an extractor based on the Soxhlet principle with a mixture of 80–85 per cent benzene and 15–20 per cent of crude wood alcohol. The extract is evaporated, the solvent distilled and recovered, leaving the crude montan wax, which is then steam distilled to remove the last trace of solvent. It contains about 70 per cent of wax, 15 per cent of resin, and 15 per cent of bitumen. The residue in the extractor is briquetted with pitch or tar and sold as a fuel.

"The crude wax is made by the Riebeck'sche Montan Werke at the Amsdorf and Wansleben plants[19], both near Halle. It is either deresinified with alcohol and distilled at their Volpke plant at Kreis Neubaldensleben, near Magdeburg, to produce the montan wax of commerce, with oil and pitch as by-products; or, more completely extracted with a benzene-alcohol mixture to produce a 95 per cent wax suitable for conversion to the so-called

'I.G. Waxes' at Oppau and Gersthofen, by the I.G. Farbenindustrie A.G. At Amsdorf the crude wax is milled to a powder which is wetted with alcohol to prevent explosions. The powder is then heated in a vessel at 40–45°C and agitated with the mixed solvent. The resin rises to the top of the vessel where it is removed. The resin liquid is further agitated to settle out wax. The combined fraction is heated with steam outside as well as inside of the vessel to remove all of the residual solvent. The by-product resin is sold as a rosin substitute or blended with raw wax and sold to the leather industry for leather impregnation. The deresinified wax was oxidized with chromic acid-sulfuric acid solutions at the oxidation plant at Gersthofen, to produce '*I.G. Wax S.*' [The ketone and paraffin plant at Oppau was destroyed by bombing in World War II; the fatty acid and ester plant at Gersthofen is intact and again operating.]

"The oxidation plant at Gersthofen consists of a series of lead-lined cast iron kettles, jacketed and lagged, each suited to treating a ton batch of wax. The kettles can be cooled by water or heated by steam, and are fitted with agitators and bottom outlet. The vessels for holding the acid solutions are situated on a staging above the oxidation kettles, and the oxidant and spent liquor are handled in lead pipes on wooden guttering. The oxidation is carried out in batches and in three stages[28]; the first is exothermic but can be controlled without external cooling by adding the oxidant slowly over a period of 4 hours to the molten wax with agitation. In the second and third stages additional steam heating is employed, with a temperature of oxidation of 110–120°C, each stage taking 3 hours to complete, and half an hour to separate spent acid, although it is possible to work a countercurrent oxidation process with a battery of reaction vessels.

"The composition of the oxidizing liquor is 1 part CrO_3 plus 3 to 4 parts H_2SO_4, and the amount of CrO_3 necessary to each batch is not less than 1¼ parts to 1 part of wax. The spent liquors are regenerated electrolytically. The product is now treated in another vessel with sulfuric acid to remove chromium complexes, and then with water to remove the sulfuric acid, and the water removed with the aid of heat under slight vacuum. The molten wax is run off into aluminum trays where it is congealed and the hard wax, '*I.G. Wax S*,' broken by hand. It can be flaked or milled."

Composition of Specific I.G. Waxes. Much of the information given below is taken from a U. S. Department of Commerce report[19]. "*I.G. Wax OP*" is a mixture of the 1:3 butylene glycol ester and the calcium salt of "I.G. Wax S." The ester itself is of little practicable use. "I.G. Wax OP" has a saponification number of 117.8–119.9 by the International Commission method (6 hr) but a value of 187.4 by the Hezel method; the discrepancy as explained by Zöllner[56] is due to the presence of Ca soap (0.72% Ca).

"I.G. Wax E" is a glycol ester of "I.G. Wax S" containing a slight excess of the latter. It is prepared by heating together "I.G. Wax S" 2000, ethylene glycol 200, and sulfuric acid 0.2 parts. The molten mixture is agitated for 10 to 12 hours at 120°C.

"I.G. Wax S," the manufacture of which has been described, consists essentially of 85 per cent of a mixture of C_{26}–C_{30} acids (montanic acid from the hydrolysis of the original esters, monobasic acids from the oxidation of the wax alcohols split off during hydrolysis, and about 20 per cent of dibasic acids from —OH–containing esters) and 15 per cent of unreacted esters. A similar product made by milder oxidation of the extracted montan wax is *"I.G. Wax L,"* which contains a little more of the unreacted esters.

"I.G. Wax BJ" is a mixture of the ethylene glycol esters of equimolecular proportions of "I.G. Wax S" and other fatty acids such as stearic and palmitic, modified by the addition of soft paraffin wax.

"I.G. Wax Z" is a microcrystalline hydrocarbon of 55 carbon chain length, which was manufactured at Oppau by ketonizing "I.G. Wax S," or "I.G. Wax L," or both, and then reducing the ketone with hydrogen to the hydrocarbon in accordance with the Jahrstorfer method of preparation. "I.G. Wax Z" now has only historic significance since from an economic standpoint it is being replaced in the industries by a similar wax produced by the Fischer-Tropsch synthesis.

"I.G. Wax CR" is the butylene glycol ester of a mixture of montanic acid and raw montan wax. It is blackish-brown in color. It melts at 80.8°C, and solidifies at 74.1°C, and has a specific gravity (d^{20}) of 1.006. It has a saponification number of 123.9, and contains 12.05 per cent of unsaponifiable matter. Its common use is as a hardening agent for other waxes; the addition of 5–10 per cent is effective. It is claimed that the addition of 18 per cent of I.G. Wax CR to other waxes will make them as hard or harder than carnauba wax.

"I.G. Wax V" is a wax with a high degree of solubility in turpentine and its substitutes, and is capable of producing an excellent luster. The wax itself is brittle and has a lustrous appearance.

Properties of "Gersthofen Waxes." The analytical constants of "Gersthofen Waxes" as produced by Werk Lech-Chemie (Farbwerke Hoechst A.-G.) are listed at the top of following page,

In Germany most of the "I.G. Waxes" are being made in Gersthofen by Werk Lech-Chemie Gersthofen, and a far smaller amount at Oppau, Ludwigshafen by the Badische Anilin- & Soda-Fabrik. The series includes OP, Special, E, KPS, S, L, KP, CR, BJ Bleached, BJ Unbleached, and the newer ones, O, OM, and F. These "Gersthofen Waxes," with the exception of the last three, are substantially the same as the "I.G. Waxes" of similar numbers.

Type	Melting Point (°C)	Melting Point (°F)	Acid Value	Saponification Number	Color
OP[a], O[b]	102–106[g]	216–223	10–15	110–125	very pale yellow
OM[a]	95–100[g]	203–212	17–22	110–125	very pale yellow
F[b]	73–76	163–169	6–10	95–105	light yellow
Special[a]	98–102	208–225	13–18	95–110	dark brown
E[d]	78–82	172–180	15–20	155–175	almost white
KPS[d]	80–83	166–181	20–30	135–150	light yellow
S[d]	80–83	166–181	145–160	165–185	almost white
L[e]	80–83	166–181	125–145	150–170	pale yellow
KP[d]	80–83	166–181	20–30	130–145	reddish yellow
CR[d]	82–85	180–185	30–35	115–130	blackish brown
BJ—Unbleached[f]	70–73	158–163	17–25	135–150	light yellow
BJ—Bleached[f]	70–73	158–163	68–85	155–170	pale ivory
V	48–50	118–122	0	0	snow white

[a] hard, noncrystalline; [b] hard; [c] hard, fine crystalline; [d] hard, crystalline; [e] very hard, crystalline; [f] soft, crystalline; [g] dropping point (Ubbelohde); [h] wax O differs from OP in oil absorption ability, and in use is blended with wax E.

"Gersthofen OP" is the butylene glycol ester of Wax S (see "I.G. Wax S" for its preparation) saponified with calcium hydroxide; *"Gersthofen Wax S"* is essentially a wax of high montanic acid content in the free state, and is highly saponifiable. When treated with alkaline reagents Wax S itself will emulsify to produce snow-white emulsions. *"Gersthofen Wax L,"* a somewhat similar product, has a saponification number of 150.8 to 152.4.

"Gersthofen Wax KPS" is an oxidized mixture of deresinified and raw montan wax, esterified with a mixture of ethylene and butylene glycol. *"Gersthofen Wax KP"* is the glycol ester of Wax S. Wax L referred to above is made by a milder oxidation process than Wax S. *"Gersthofen Wax CR"* is the butylene glycol ester of a mixture of Wax S and raw montan. *"Gersthofen Wax Special"* is the butylene glycol ester of a mixture of raw montan and a Wax S saponified with calcium hydroxide, as described by Sayre and Marsel[49].

The output of "Gersthofen Waxes', has been estimated to approach 800,000 pounds for 1955, much of the product being consumed in Europe. The prices in the United States range from 54 to 80 cents per pound.

Uses. "Gersthofen Waxes" OP, O, and OM, because of their excellent hardness, solvent absorption and retention properties, are valued constituents in polishes of the paste type. They have proved successful in polishes of the liquid type. "Gersthofen Wax V" in combination with other waxes, like OP, OM, and F, has formed a definitely good foundation in liquid polishes for floor, furniture, and motor car use.

"Gersthofen Wax S" is recommended for the hardening of composition candles made from paraffine and stearic acid. A small proportion of Wax S incorporated in the candle composition will prevent decorative or other

candles from bending under the hottest climatic conditions. Wax S will also produce white polish emulsions.

"Gersthofen Wax F" is a new type of hard ester wax of good gloss-giving and solvent-binding properties. It is a valuable component in floor polish; floor stain; liquid floor polish; shoe polish, uncolored and colored; and black shoe polish. In these formulations Wax F is generally used in conjunction with one or more of the waxes O, OM, OP, or V; paraffine; and ozocerite.

"Gersthofen Wax L" is used in shoe manufacturing for finishing purposes and as a shoe last wax; also as a stiffening agent for lubricating greases. Type KP is especially designed for use in carbon paper foundations. Type "KPS" is used as a back surfacing agent for carbon paper to prevent recurling. It is also used in conjunction with carnauba wax, "Durez" resin 219, oleic acid, and "Morpholine" in producing so-called self-polishing, dry-bright water emulsions.

(5) ALKYL ESTERS AND POLYHYDRIC ALCOHOL ESTERS OF 12-HYDROXYSTEARIC ACID

Alkyl Esters of 12-Hydroxystearic Acid

The normal primary C_1 to C_8 alkyl esters of 12-hydroxystearic acid are prepared by refluxing the acid for about 8 hours with a large excess of the anhydrous alcohol containing about 6 to 8 per cent of dry hydrochloric acid. The normal, primary, even-numbered C_8 to C_{18} alkyl esters are prepared by refluxing the acid with an equivalent or twofold excess of the alcohol in benzene in presence of 5 per cent of benzene sulfonic acid (on the weight of the acid) as catalyst. The melting points and solubilities have been recorded by Bell and Taub[5]. These esters may be used in the formulation of waxes which are stable and free from color, odor, and rancidity. Alkyl esters C_{10} to C_{18} melt at 56 to 76°C; they are sparingly soluble in ethanol, acetone, ligroin, and oils, but are very soluble in toluene, except the C_{16} and C_{18} alkyl ester.

Commercial *methyl hydroxystearate*, the C_1 alkyl ester of 12-hydroxystearic acid, has been marketed by the Baker Castor Oil Company, New York, under the trade name of "Paracin 1." It is essentially a castor oil derivative. It has an average molecular weight of 312, acid value 4, saponification number 177, iodine number 5, and melting point 48°C. Paracin 1 is a white waxy solid produced in the form of short, flat rods. It is useful in the preparation of multipurpose greases, and as a plasticizer for nitrocellulose, allyl starch, and synthetic waxes.

Octadecyl 12-Hydroxystearate Wax

According to the specifications of Snell and Guiteras[58] described in a patent issued to these investigators in 1945, 144 parts of hydroxystearic

acid from hydrogenated castor oil and 120 parts of octadecyl alcohol from reduction of stearic acid are melted together with 1 part of commercial paratoluene sulfonic acid. In 2 to 4 hours at 110–120°C with slow stirring the acid value drops to about 4.4. The catalyst may be washed out or neutralized, giving 241 parts of *octadecyl 12-hydroxystearate* (m. 71°C), and recrystallized from warm ethanol to give a product of 73°C melting point. They state that if the alcohol or acid of the straight-chain series (16–24 C atoms) carries one hydroxyl group the ester formed closely approximates the properties of a natural wax, and that straight chains are preferable to branched chains.

Similarly stearic acid and 1,12-octadecanediol give *12-hydroxyoctadecyl stearate*. Octadecanediol (m. 65–67°C), according to Shinosaki and Kubo[51] is the principal constituent of a waxlike product obtained by hydrogenating castor oil at a high temperature (250°C) and pressure (80 kg per sq cm), employing copper as a catalyst; or at 220–223°C under 100 kg per sq cm pressure when using cobalt as the catalyst. In hydrogenating, the hydroxy linkage of the acyl group of ricinoleic acid and its ester can be reduced. Octadecanediol when recrystallized from alcohol melted at 71.2°C.

Polyhydric Alcohol Esters of 12-Hydroxystearic Acid

Glycol esters of 12-hydroxystearic acid may be prepared by refluxing the acid with an excess of glycol, with the aid of a catalyst, preferably toluene-*p*-sulfonic acid. The acid itself may be isolated from hydrogenated castor oil by the method of Jakes and Hökl. Bell and Taub[6] determined the condition of time and temperature required for the esterification which would result in the best yield of most nearly pure monoesters.

The *ethylene glycol monoester* is prepared by refluxing 12-hydroxystearic acid 50, xylene 50, ethylene glycol 103.5, and catalyst 0.25 parts, for 30 minutes on an oil bath at 160°C. *Propylene glycol monoester* is prepared by refluxing propylene glycol 127 parts with the same quantities of ingredients for 60 minutes at 160°C. *Trimethylene glycol monoester* is prepared by refluxing *12*-hydroxystearic acid 30 parts (0.1 mol), xylene 60 parts, trimethylene glycol 76.1 parts (1 mol), and catalyst 0.15 part (0.5% of wt. of acid), for one hour on an oil bath at 160°C.

Bell and Taub[6] in their experiments of producing glycol esters of *12*-hydroxystearic acid found that the *ethylene glycol diester* is a hard, brittle, noncrystalline material which melts at 90–92°C, and has a hydroxyl (OH) value of 175 (theoretical 175.1). These synthetic products may generally be described as solid esters of the nonemulsifying type, very high in melting point, free from color, and of good stability. Their use has been suggested as waxes with special properties for coatings, insulating materials, polishes, etc. Their applicability is further broadened by their ready conversion into

solid esters of the emulsifying type, making them useful in the cosmetic and pharmaceutical fields. (Also see p. 668).

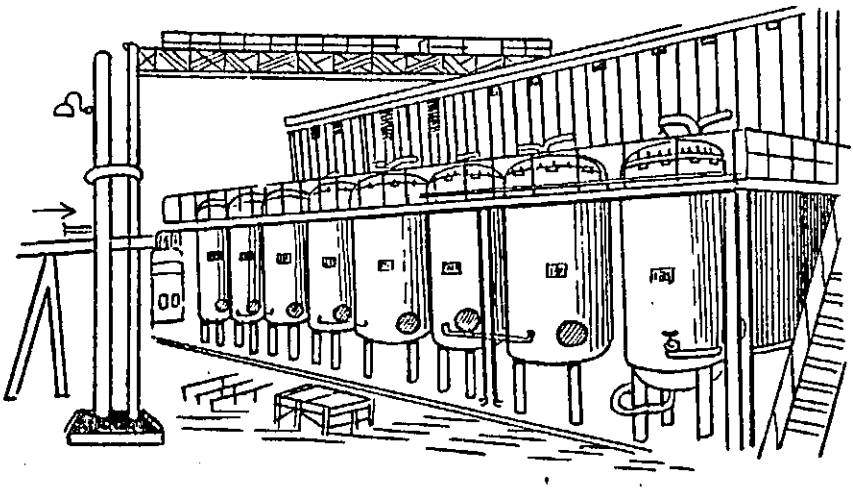
(6) SYNTHETIC HYDROCARBON WAXES

Fischer-Tropsch Waxes

Hydrocarbon waxes of very high molecular weight and melting point, and of great hardness are obtained as by-products in the synthesis of liquid fuels (gasoline and diesel oil) from carbon monoxide (CO) and hydrogen (H_2) by the Fischer-Tropsch reaction. Franz Fischer and Hans Tropsch in 1923 stated (*Brennstoff-Chem.*, **4**, 195–197) that previous investigators had carried out the reduction of CO to methane (CH_4) using finely divided nickel (Ni) and cobalt (Co) as a catalyst at 380°C, and in the presence of iron (Fe) at 500–600°C. Fischer and Tropsch undertook to study the reduction of CO in contact with Fe under pressure. Their apparatus consisted of a heavy iron tube (90 cm l x 2.1 cm i.d.) electrically heated. The reaction was studied at 2–100 atmospheres (A) pressure and at 400–430°C temperature. The gas used consisted essentially of CO and H_2. At 2A pressure only small amounts of CH_4 were formed. The highest percentage of CH_4 was formed at 44–55 A. These investigators found that water gas, freed from sulfur compounds, and then treated at 400–500°C at 150 A pressure in the presence of alkalized Fe turnings would produce an oil and water layer—the latter rich in oxygenated compounds. From the water-soluble product, designated as "pyrosynthol" could be recovered low molecular weight acids, alcohols, and ketones. The oil which was termed "synthol" (b. 80–200°C) was found suitable for motor fuel. By heating synthol at 450°C under pressure, a mixture of hydrocarbons (b. 50–300°C) of benzin type could be obtained which was termed "synthin."

In 1924 suitable autoclaves or reactors for the Fischer-Tropsch reaction were developed, with provision made to carry away the great heat developed by the exothermic reaction. In regulating the proportion of H_2 to CO it was discovered that the richer the H_2 the greater the preponderance of oxygenated compounds, and vice versa the richer the CO content of the infeed gas the greater the yield of oil, and indirectly of wax recoverable from the residue.

As the Fischer-Tropsch reaction was described by Fischer and Koch[25] in 1932, the mixed gases, H_2 and CO, were passed over a fixed cobalt-diatomaceous earth catalyst at a temperature of below 250°C and at 15 A (220 psi) pressure. The initial work of the oil circulation process system of heat exchange, in conjunction with water cooling, and close temperature control was done at the plant of the I.G. Farbenindustrie at Oppau, Germany, but was interrupted by the war. The reaction was made a continuous one limited only to the 500–2000 hours life of the catalyst.



Courtesy Dura Commodities, Inc.

FIGURE 19. Synthesis pressure reactors at Wanne-Eickel, West Germany, for the production of waxes by the Fischer-Tropsch process. Arrow at left indicates direction of feed gas into the reactors.

Hamai[24], who in his physiochemical investigations studied the catalytic mechanism with cobalt, also conducted syntheses at 250°C with Ni and Fe, and found that the catalytic reduction with Fe was so energetic that the CO reacted with the water formed to produce an appreciable amount of carbon dioxide (CO_2). In modern practice where any one of several forms of Fe is used as a catalyst the CO_2 is removed by a scrubber. Heckel[25] employed a catalyst which contained cobalt 100, manganese 15, and infusorial earth 10–20 parts by weight. He found it expedient to start out with a proportion of H_2 to CO of 2:1, a temperature of 160–175°C, and a pressure upwards of 75 psi.

The firm of Krupp Kohlechemie G. m. b. H. is operating a hydrocarbon synthesis plant at Wanne-Eickel, where low temperature coke is available in quantity to get the blue water gas needed. Government agencies in both Germany and the United States have been instrumental in further development of the F–T processes; both the Institute of Coal Research, Ruhr and the Synthetic Fuels Research Branch, U. S. Bureau of Mines, Bruceton, Pennsylvania. Ruhrchemie A.G. is reported to compress 2 volumes of H_2 to 1 volume of CO to about 7 A and pass it along a granular bed of Co catalyst at 185–205°C, to get gaseous and liquid hydrocarbons, wax, and oxygenated compounds in the water layer formed by the reaction. A mixed cobalt, thoria, magnesia on kieselguhr catalyst is said to be used. It is customary to operate the reactions in several stages, regulating the rate of flow of the inlet gas, the temperature, and the pressure; the last stage em-

ploys higher flow rates, lower H_2 to CO ratio (1½:1), and lower temperature.

The catalytic mechanism of the F-T reaction has been postulated by Hamai[24]; it would seem that CO is adsorbed or displaces H_2 adsorbed on the cobalt (Co) surface, forming Co—Co—(—C═O) Co, or, taking the cobalt linkages as unity, simply Co (—C═O). The latter is reduced by adsorbed H_2 to Co (—HCOH), then to Co (—CH_2). The CH_2 groupings adsorbed on the Co surface migrate freely over the surface to form Co (—$CH_2CH_2CH_2CH_2$. . .) which, upon desorption, yield $(CH_2)_n$ and finally liquid products by hydrogenation.

In 1946 Friedman[26] (Phillips Petroleum Company) discovered that contrary to what might be expected from a knowledge of the prior art, when the CO-H_2 feed to a Fischer-Tropsch conversion contains more than 40 per cent of an inert diluent, unusually high yields of normally solid hydrocarbons are obtained. In addition the yield of gasoline is as high as that obtained from feeds which contain little or no lube oils, and of better quality. The feed gas which contains CO and H_2 in a mol ratio of about 1:2, is diluted with a sufficient amount of the inert diluent such as nitrogen (N_2), methane (CH_4), or CO_2, e.g., a suitable composition of feed gas is 50 N_2, 16 CO, and 34 H_2 parts by volume. One convenient method for preparing feed gas is by partial combination of CH_4 with air in the presence of a nickel catalyst; the effluent gas than contains approximately 40 per cent N_2, as well as CO and H_2 in a mol ratio of about 1:2.

The feed as described is then passed to a reactor, or series of reactors, in the presence of the catalyst. Friedman prefers a cobalt-containing catalyst such as one consisting of metallic cobalt 100, thoria 18, and Kieselguhr 100 parts. When this catalyst is used suitable reaction conditions are: pressure, about 100 psi; temperature, about 200°C; space velocity, 100 to 200 volumes per volume of catalyst per hour. With a vertical type of reactor the wax may be continuously drained. The reactor is provided with suitable cooling means for temperature control. The wax in the gasoline-free residue attains an optimum of 50 volume per cent with 50 volume per cent of nitrogen in the feed, in a run of 63 hours and space velocity of 100–170 vol/hr.

Modern Production of "F-T Waxes." In the Fischer-Tropsch reaction the removal of the high exothermic heat of reaction is, according to Benson and his co-workers[8] of the U. S. Bureau of Mines, activated by sensible heating of a recycle oil that completely submerges the catalyst so that close temperature control can be obtained. The temperature of the reactor is maintained at 235–255°C, with a pressure at 300–450 psi. The feed gas ratio is 1:1 for the hydrogen-carbon monoxide mixture. The proportion of the gases ranges from 0.7 to 1.3 H to 1 CO, depending upon the type of fuel oils desired and the economics of the operation. The life of the catalyst

is shortened with a reduction in the proportion of hydrogen, and the amount of wax is increased but only at the expense in the decreased output of gasoline. With a 1:1 ratio the total wax yield is 9.6 to 13.8 per cent[8]. The reactor can be operated continuously for about 2000 hours before the fused iron catalyst is spent[8].

At the Krupp plant the reaction process is employed primarily to make gasoline, but hard paraffin waxes to the extent of 5–10 per cent are produced as a by-product, when the higher boiling synthetic paraffin oils or heavy distillate is subjected to chilling. The paraffin wax obtained has a melting point of 50°C (122°F) and consists chiefly of the hydrocarbons $C_{17}H_{36}$ to $C_{25}H_{52}$. The catalyst itself acts as a carrier and becomes saturated with wax melting at a much higher temperature, namely 70 to 80°C, of which an ether-soluble portion melts at 92°C. By distillation in a vacuum still it is possible to separate the contact wax into waxes having melting points of 100°C and 105°C, which are commercially known as "Ruhrwachs"—*"Type EH 100"* and *"Type SH 105,"* or as "FT Wax 200" and "FT Wax 300" respectively, in the American market.

Composition of "F-T Waxes." In 1935 Koch and Ibing[39] attempted to determine the composition of the synthetic hard wax (m. 80°C) produced by the Fischer-Tropsch synthesis by separating the individual high molar hydrocarbons by means of high vacuum distillation. They used a micro apparatus for distillations based upon the principle of the molecular still of Carothers, an improvement over that of Washburn, and perfected in design by Gilchrist and Karlik. By this means they were able to separate the C_{20}, C_{30}, and C_{40} hydrocarbons. A portion melting between 102°C and 112°C was distilled at 10 to 25 mμ mercury to obtain normal paraffins, C_{50}, C_{60}, and C_{70}. At 300°C evidence of cracking appears, so that the 110° to 114°C melting point residue could not be investigated further.

The raw wax for the distillation was obtained by extracting the Ni-Mn-Al catalyst, used in the water-gas reaction (Fischer-Tropsch), for several weeks with benzene. The extraction was carried out altogether in three successive stages, and the dark-colored paraffins were bleached with bleaching-clay at 100°C to yield straw-colored odorless products:

Test	M.P.	Av. Mol. Wt.
1	70°C	570
2	80°C	630
3	90°C	740

They extracted 100 grams of the synthetic wax with 750 cc of ether, and after evaporating to a small volume added alcohol to precipitate snow-white crystals, which were filtered on a suction filter, washed free of solvent, and dried. In this way hard paraffins of 88°C, 98°C, and 106°C melting points were obtained. The molecular weights were 700 and 860 for the 88°C and 98°C melting point waxes respectively. The ether-soluble portion gave

waxes of 40°C and 60°C melting points with molecular weights of 490 and 610 respectively, by the Rieche method.

Certain fractional extractions with chloroform and treatment with dichloroethylene led to the separation of hard paraffins of 112° and 116°C melting points, having molecular weights of 1750 and 2140 respectively. The chloroform-insoluble residue with molecular weight of over 2000 appeared to be composed of paraffin molecules of approximately 150 carbon atoms. It is postulated that the optimum melting point of the Fischer-Tropsch will not exceed 118°C for the largest molecule, and is that of a *normal* paraffin rather than an *iso*-paraffin. These high molar paraffins show a very high dielectric strength.

The molecular weight of several fractions is compared with that of the normal paraffins of similar melting point in the tabulation below by Koch and Ibing[49].

Fraction No.	M.P. (°C)	Mol. Wt.	*n*-Paraffin	M.P. (°C)	Mol. Wt.*
l-d	81.3–81.8	561	$C_{40}H_{82}$	80.5–81	563
v-f	95.5–96.4	766	$C_{54}H_{110}$	95	759
vl-f	101.5–102.1	895	$C_{64}H_{130}$	102	899
B-s	91.5–92.5	687	$C_{50}H_{102}$	91.9–92.3	703

* Calculated molecular weight.

Koch and Ibing[49] found that synthetic paraffin wax (m. 80°C) is completely soluble in amyl alcohol, ethyl acetate, petrolic ether, benzene, toluene, xylene, carbon tetrachloride, and certain other solvents. It is partly soluble in propyl alcohol, ether, chloroform, and dichloroethylene, and insoluble in methanol, ethanol, acetone, and methyl ethyl ketone.

These normal strength chain paraffins of very high molecular weight (570 to 740 plus) are considered of great value in a number of applications such as for use in dielectric, impregnating, and coating compositions, and as intermediates in the preparation of various useful materials such as those obtained by oxidation, cracking, or dehydration. Such useful materials include fatty acids of sufficiently high molecular weight to be esterified by glycerol to form glycerides as substitutes for natural fats of food value.

A *contact wax* (designated # 1889) produced by the Fischer-Tropsch synthesis and offered in the New York market consisted of pure white hard flakes. Upon melting the wax is of a creamy white color. It has a melting point of 103.8°C, Ball-and-Ring 87°C, softening point (Ring-and-Plunger) 73°C, softening point (Fisher-Johns) 58°C, melting point (Fisher-Johns) 103°C. The penetration reading (100 g/5 sec/25°C) is 9.2. The spread between the softening and melting points by the Fisher-Johns method is 98°C, indicating a very wide range of hydrocarbons, possibly extending from C_{24} to C_{150}, or from a molecular weight of 340 to 2140, with an average of 940.

(7) HYDROGENATED WAXES

Hydrogenation of Oils

Hydrogenation of liquid fats in the presence of such catalysts as nickel, copper, platinum, or palladium into more solid fats, a development first introduced about 1911, has revolutionized the tallow industry. Several processes are used: (1) the agitation process* in which mechanical agitation is used to obtain intimate contact between the liquid fat, the hydrogen, and the catalyst; (2) the injection or circulation process in which the liquid fat and catalyst are taken from the lower part of the reaction end and injected as a fine spray into a gas-space at the top; (3) the continuous process in which the liquid fat passes down over a stationary catalyst while a current of hydrogen is forced up through the chamber.

The hydrogenation of oils can be so controlled that the oil is hardened to a definite iodine number or to a definite refractive index number. Since hydrogenated oils are for the most part merely hardened fats only brief mention is made of them here. With hydrogenation the oil loses its oily characteristics and the iodine number decreases with a corresponding increase in the melting point of the material. It is not possible to secure the same kind of tallow from several different kinds of vegetable oils even by carefully controlling the degree of hydrogenation. There is perhaps a closer approach to animal tallow with hardened whale oil than with other hardened oils. The Germans use a considerable amount of hardened whale oil for food purposes. The approach of imitation to real tallow is interestingly set forth in these figures:

	Iodine Number	Melting Point (°C)
Beef tallow	35.5	43–44
Hardened linseed oil	35.5	57.0
Hardened cottonseed oil	35.5	51.0
Hardened whale oil	35.5	47.5
Mutton tallow	42.5	45.0
Hardened linseed oil	42.5	55.0
Hardened cottonseed oil	42.5	48.2
Hardened whale oil	42.5	45.4

* In the Woltman method [British Patent 112,293 (1916)] the material and catalyst are agitated together by rotary perforated arms through which hydrogen is injected. A horizontal steam-jacketed receptacle contains a hollow rotary horizontal shaft through which hydrogen is passed from a pipe and from which it escapes by perforated arms. The duration of content between the gas and the fat may be regulated, either by providing perforations in one side of the arms only and rotating the arms so that the gas is injected either in or against the direction of rotation, or by dividing the arms by partitions to form longitudinal gas passages which may be separately supplied with gas.

Should we reduce the iodine number of cottonseed oil to 20 by hydrogenation, the melting point would be 56°C, the product waxlike and easily flaked, suited to meet individual industrial needs, but obviously prohibitive as a substitute for beef tallow. Refractive indices of the synthetic fats are directly proportional to the iodine numbers as can be shown by straight line curves. Hence a determination of the refractive index will give the iodine number for a hydrogenated oil of known purity. A determination of the refractive index is simpler than that of either iodine number or melting point as a control for the degree of hydrogenation.

Hydrogenated Vegetable Waxes

Cottonseed oil, soybean oil, peanut oil, and corn oil can be hydrogenated to a low iodine number whereby waxlike products are produced. Hydrogenated cottonseed oil has been marketed as "Coto Flakes"; they are beautiful flakes, pure white, odorless and tasteless. Since the principal constituent is *tristearin*, this waxlike product is easily saponified, as are the other hydrogenated vegetable waxes.

Hydrogenated cottonseed oil has been used as a protective covering for molten tin through which the pickled steel sheets are coated in the manufacture of dipped tin plate, but has now been largely superceded by *hydrogenated fish oil* (see Hydrogenated Marine Oil Waxes, p. 473). The advantage of a hydrogenated oil over palm oil used for the purpose is that it is far less likely to become rancid in the prolonged heating of the molten bath of tin. Most of the output of hydrogenated edible vegetable oils is used in edible products.

By hydrogenating castor oil at 180°C optimum with a nickel catalyst, a diaphanous waxlike material can be produced, which solid is roughly comprised of trihydroxystearin (m. 89.4°C) 5, stearodihydroxystearin (m. 74.9°C) 10, and distearohydroxystearin (m. 69.5°C) 75 parts. The product is referred to as *hydrogenated castor oil*. More fully hydrogenated products are described below.

A commercial form of fully hydrogenated castor oil in either flake or powder is produced by the Baker Castor Oil Company, New York, under the name of "Castorwax." Eighty-five per cent of its fatty acid groups have the hydroxyl group characteristic of castor oil. "*Opalwax*," similar to "*Castorwax*," is a brand name given to a synthetic wax of the E. I. du Pont de Nemours & Company, Inc., produced by the catalytic hydrogenation of castor oil. "Opalwax" is said to consist principally of 12-hydroxystearin (glyceryl trihydroxystearate, or trihydroxystearin). The production of "Opalwax" has been discontinued. There are at least five firms in the United States producing similar waxes. It was estimated that 5½ million pounds of hydrogenated castor oil waxes were produced in 1950.

The flakes of the waxlike products described are produced by a flaking machine. One type of machine consists of a hollow polished stainless steel cylinder, which can be cooled by circulating cold water, with the intake and output at the ends of the horizontal axis. The molten wax is applied to the periphery of the cylinder from a rectangular melting vessel with a longitudinal gate valve. The solid wax film is removed from the cylinder by a doctor blade. The congealed wax film may then be readily crunched into flakes.

"Castorwax" (*12-hydroxystearin*) is white in color in its solid form and straw-colored in molten form. It has a melting point of 86°C (186.8° F); it softens at only one degree F lower than its melting point. "Opalwax," which closely resembles "Castorwax," has been described as odorless and tasteless, pearl-white in color, of dull vitreous luster, choncoidal in fracture, and nontoxic. It has a durometer hardness of 100 at 25°C or below.

The specific gravity of 12-hydroxystearin changes appreciably with changes in temperature as is shown below:

Temperature (°C)	Specific Gravity $\left(\frac{4^{t}}{4^{t}}\right)$
24	0.9896
35	0.9857
90	0.9030
100	0.8960
113	0.8870
130	0.8790

When cast in a chilled mold it has a density of 1.000 at 20°C. It has a coefficient of cubical expansion of 0.000784 between 86 and 110°C; 0.000679 between 110 and 120°C; and 0.000455 between 120 and 130°C.

12-Hydroxystearin is soluble to the extent of less than 1 gram per 100 ml at 18–33°C in the following solvents: isobutanol, "Cellosolve," methanol, petrolic ether, and methyl "Cellosolve." The solubility of "Opalwax" in various solvents as given by the Ammonia Department of E. I. du Pont de Nemours & Company, Inc., is as follows:

SOLUBILITY OF "OPALWAX" IN GRAMS PER 100 SOLVENT

Solvent	At 18–20°C	At 30°C
Toluene	1.5	1.5
Carbon tetrachloride	1.4	1.5
Carbon bisulfide	1.3	1.9
Xylene	1.2	1.2
Acetone	0.6	1.1
Ethyl ether	0.3	1.2
Glacial acetic acid	0.4	1.2
Ethanol (95%)	0.05	0.40 (33°C)

"Opalwax" was reported to have an acid value of less than 2.0, saponification number 175–185, iodine number 2.5–8.5, hydroxyl number 155–165, and ash content less than 0.005 per cent. Its dielectric constant is about 12 at 30°C, and 22 at 60°C for 100 cycles.

12-Hydroxystearin when added to other waxes tends to greatly elevate their melting points, partly through greatly increasing the sluggishness of melting of the wax mixture.

In making emulsions of 12-hydroxystearin with water the molten wax at about 100°C is introduced, with rapid agitation, into about two and a half times its own weight of water (85°C) in which a small amount of a suitable emulsifying agent (polyvinyl alcohol) has been thoroughly mixed in advance. The emulsion will remain stable when subsequently diluted and yield a continuous film upon drying.

12-Hydroxystearin is used extensively in the preparation of multipurpose greases that combine high temperature stability with outstanding water resistance. For such lubricants, suited to drawing or rolling metals, etc., it is first converted into its lithium salt, *lithium hydroxystearate*. Such greases are produced under a basic patent held by the Foote Mineral Company and Shell's process patent.

The Baker Castor Oil Company lists the physical characteristics of "Castorwax" which make it of value in many formulations such as adhesives, candles, crayons, foundry waxes, gasket impregnant, grease lubricant, hot melt compounds, leather coatings, metal working, mold lubricants, packings, paper coatings, polishes, potting compounds, rubber compounding, sealants, textile finishing, and transfer inks. These characteristics are extreme insolubility; high, sharp melting point; hardness; nontoxicity; good dielectric; resin and wax compatibility; waterproofness; non-yellowing white; greaseproofness. It is also suggested as a chemical intermediate in possible reactions which involve acylations, isocyanate coupling acetalization, oxidation, esterification, sulfation, and saponification.

When powdered 12-hydroxystearin is mixed with fine materials to be molded or tableted, it proves definitely superior to stearic acid or tristearin for that purpose. It is useful as the chief ingredient in gasket compounds that must resist gasoline.

Hydrogenated Marine Oil Waxes

Marine oil, such as that of the Arctic finback whale, can be hardened by high hydrogenation. The resultant product contains about 95 per cent of free fatty acids. These acids consist of myristic (6%), palmitic (34%), stearic (30%), arachidic (19%), behenic (5%), and lignoceric (0.5%). Hydrogenated marine oil has been used for the same purpose as palm oil as a covering agent for molten tin from which the dip tin coated sheet

emerges in the manufacture of tinplate. A commercial product is "Hydrogenated Marine Fatty Acid No. 52" (*52* indicating a titer of 51–52°C) made by Swift & Company. Its properties are given as free fatty acids (FFA) 95 per cent, color 14–15 (FAC), saponification number 200, iodine number 6 max., acid number 194. The product is advertised as having a good dispersibility in rubber products. Another hydrogenated fish oil used as a substitute for palm oil by fabricators of tin plate is known as "Hydrofol Tinfat 25."

Hydrogenated sperm oil is marketed in semisolid and solid grades, the latter resembling spermaceti. The chemical components, free and combined, consit of *saturated fatty acids*, C_{10}–C_{22}, the C_{16} and C_{18} acids predominating; *unsaturated acids*, namely lauroleic, myristoleic, palmitoleic, oleic, gadoleic, and erucic acid; *saturated alcohols*, namely myristyl, cetyl, and stearyl alcohol; and *unsaturated alcohols*—palmitoleyl, and oleyl alcohol. For example, the commercial hydrogenated sperm oil known as "Spermafol 45" (m. 45–46°C) contains 12–13 per cent of unsaturated acids, whereas "Spermafol 52" (m. 50–52°C), a more expensive and harder grade, contains only 3–3½ per cent of unsaturated acids. *"Spermafol 45"* contains about 13–14 per cent of unsaturated alcohols, whereas *"Spermafol 52"* because of the greater degree of hydrogenation contains only 3 per cent of unsaturated alcohols. Both contain 33–38 per cent of unsaponifiable.

Higher Alcohol Waxes

A mixture of higher alcohols corresponding to the acyl radicals of coconut oil was produced in 1914 by Normann[42] by the catalytic hydrogenation of coconut oil at 285°C under about 250 atmospheres pressure with the aid of a cobalt-containing catalyst. Guyer[32] in 1938 used a catalyst of chromium oxide or copper oxide containing about 1per cent of iron to produce synthetic waxes from coconut fat and from sperm oil. In some instances, e.g. *cetyl palmitate* (spermaceti), aliphatic monohydric alcohol esters could be converted to wax alcohols. He employed a temperature of 200 to 300°C and a hydrogen pressure of 150 to 300 atmospheres. According to an earlier British patent (1933) held by E.I. du Pont de Nemours & Company, Inc.,[20] the reduction from fat or fatty oil to alcohols is effected by treating the substance with an excess of hydrogen at 200 to 400°C and 105 to 205 atmospheres in the presence of a mixed cadmium-copper-zinc chromite catalyst. In this way, palm, coconut, and castor oils may be converted to waxlike products.

Green[30] carried out the reduction to alcohols by passing a rapid stream of hydrogen at a pressure of about 25 atmospheres, through a vigorously agitated mixture of the substance to be treated and a suitable catalyst. The alcohols as they formed are carried out of the reaction vessel in the stream of hydrogen.

(8) WAXY KETONES

The dialkyl ketones, generic formula $(C_nH_{2n+1})\cdot CO$ are generally prepared by the catalytic decarboxylation of the corresponding monocarboxylic acids. The higher members are all waxlike solids. This splitting off of the CO_2 group elevates the melting point beyond that of the corresponding acid.

A comparison of the melting points of laurone (14), palmitone (16), and stearone (18) with those of the corresponding acid—lauric, palmitic, and stearic—is given below.

Number of Carbons	Chemically Pure		Commercial	
	Acid	Ketone	Acid	Ketone
14	44°C	68°–69°C	37°–38°C	67°C
16	63°C	83°C	58°C	76.5°C
18	70°C	87°–88°C	67°C	80°C

In their commercial preparation the reaction is ordinarily carried out in an esterifying type of equipment under a blanket of nitrogen, to preclude the formation of metallic soap in deference to the formation of ketone. The reactor is charged with high test fatty acid, and the powdered catalyst is spread on a carrier which is either silica gel or fuller's earth. Suitable catalysts for conversion of the acid to the ketone may be found in nickel, iron, tungstic sulfide, and alumina. Iron is ordinarily employed. The temperature range is between 200° and 370°C optimum, and the time of reaction takes several hours, both varying with the chain length of the ketone prepared.

The melting points of the dialkyl ketones of the even carbon series of saturated straight-chain fatty acids are recorded below. The melting points of commercial ketones are appreciably lower than those given here.

Name	Melting Point (°C)	Name	Melting Point (°C)
Hexanone	14–15[a]	Behenone	92
Octanone	41–43[a]	Cerotone	95[d]
Caprone	58–59[a]	Montanone	97[d]
Laurone	69[a], 68–69[b]	Melissone	99.5[d]
Palmitone	82[a]	Laccerone	104
Stearone	87–88[c]	Geddione	109

[a] Petrov *et al.* (1935). [b] Briese and McElvain-hydrolysis of keto esters (1933). [c] Franke (1949).

Various yields, heating cycles, times of reaction, and types of catalysts have been reported by investigators. Grün *et al.*[31] heated *stearic acid* for six hours at 300°C in the presence of SiO_2, CuO, ZnO, TiO_2, and ThO, and obtained 7 per cent ketone; CdO gave 13 per cent; Fe oxides, Al_2O_3, Mn on kieselguhr gave 17–24 per cent. *Palmitic acid* is said to act quantitatively

with respect to yielding ketone in a period of three hours at 295°C; *myristic acid* acts similarly at 285°C. Petrov *et al.*[44] secured a 35 per cent yield of *laurone* by the action of *tert*-butyl-magnesium chloride on ethyl laurate by heating in xylene 5 hours at 110–120°C, hydrolysing with HCl, and distilling the laurone (m. 69°C, oxime m. 39–40.5°C). A similar reaction with ethyl palmitate at 110°C produced a good yield of palmitone (m. 82°C, oxime m. 59–60°C).

Stearone. Stearone is also known as 18-pentatriacontanone and has a symmetrical structure:

$$CH_3(CH_2)_{16}—\overset{\overset{O}{\|}}{C}—(CH_2)_{16}CH_3$$

In its preparation in the laboratory, excellent results are obtainable by using the classic Pipping's method in which the higher fatty acids are decomposed by phosphorous anhydride, P_2O_5, with the evolution of CO_2 and water, and the formation of ketone:

$$2RCOOH \rightarrow R_2CO + CO_2 + H_2O$$

Stearone may be produced on a small scale as follows: 9.5 g of pure stearic acid are heated in a glass vessel at 210°C with 5 g of P_2O_5, adding small portions at a time with constant stirring. At first, considerable effervescence takes place owing to the liberation of CO_2. At the end of the operation the brown mass is allowed to cool, and then gradually stirred with water to convert the residual P_2O_5 to phosphoric acid. After adding an excess of sodium hydroxide the mixture is warmed gently, stirred frequently for about 15 minutes, allowed to cool, and diluted with water. The stearone at the top of the liquid may then be separated by decantation or filtration. The yield is over 27 per cent.

Pure stearone is almost white in color, although straw-colored in its molten state. It boils at 345°C at 12 mm pressure. In its solid form it is very hard. It will not adsorb water. Stearone is sparingly soluble in organic solvents in the cold; 1.1 g of stearone will dissolve in 100 g 96 per cent alcohol. It is easily dissolved by hot organic solvents. It is miscible with paraffin wax in all proportions.

Stearone made from triple-pressed stearic acid has a lower melting point than its palmitone constituent. It melts at 78.5°C, whereas palmitone, $CH_3(CH_2)_{14}\cdot CO\cdot(CH_2)_{14}CH_3$, melts at 82°C.

Ketones Other Than Stearone

Laurone, $CH_3(CH_2)_{10}\cdot CO\cdot(CH_2)_{12}CH_3$, also known as 12-tricosanone, is a constituent of the waxy substance of haircapmoss, *Polytrichum juniperum* Hedwig. *Myristone*, also known as 14-heptacosanone, $CH_3(CH_2)_{12}\cdot CO\cdot(CH_2)_{12}CH_3$, is found to the extent of 0.23 per cent in dry alfalfa. *Palmitone*, also known as 16-hentriacontanone, $CH_3(CH_2)_{14}\cdot CO\cdot(CH_2)_{14}CH_3$, is found

in the leaf of the white sandalwood, *Santalum album* L., which also contains d-10-hydroxypalmitone, $CH_3(CH_2)_{14}\cdot CO\cdot(CH_2)_5CHOH(CH_2)_8CH_3$. Mogusa wax contains palmitone. An extraction of the hairy layer (mogusa) on the leaves of a small aromatic shrub, *Artimisia vulgaris* L., with ethyl ether yields 2.3 per cent of wax (m. 65°C), which is comprised of palmitone (m. 68.5°C), 1-eicosanol, tricosanol, and C_{10}, C_{16}, and C_{18} fatty acids. *Montanone*, $(C_{27}H_{55})_2CO$, can be prepared from montanic acid (m. 86°C) by gradually heating the acid to 200°C for a long period of time in an inert atmosphere, which causes the CO_2 to split off. Easterfield and Taylor[18] heated montanic acid with iron filings at high temperatures—up to 370°C—to produce montanone (m. 97°C). By the same method they prepared *cerotone*, $(C_{25}H_{51})_2CO$, and *melissone*, $(C_{29}H_{59})_2CO$ (m. 99.5°C). They isolated *oleone*, $(C_{17}H_{33})_2CO$ (m. 59.5°C), from the commercial oleic acid which had been heated in iron kettles. These investigators also prepared *elaidone*, $C_{35}H_{66}O$ (m. 70°C), and *brassidone*, $C_{43}H_{82}O$ (m. 80°C).

Commercial Aliphatic Ketones

The waxlike ketones which are manufactured on a large production scale are *stearone*, *laurone*, and *palmitone*. They are made from high test stearic, lauric, and palmitic acids respectively. The Fisher-Johns melting points of the higher melting commercial ketones are of the following order:

	Minimum*	Bulk	Maximum
Laurone	55°C (131°F)	66.5°C (151.7°F)	67.5°C (153.5°F)
Palmitone	60°C (140°F)	79°C (174.2°F)	80°C (176°F)
Stearone	75°C (167°F)	82°C (179.6°F)	85°C (185°F)

* The minimum melting (or softening) point indicates the presence of lower melting impurities. Substantially all of the material melts at the so-called bulk melting point.

The hardness of the commercial ketones is as follows:

	Durometer Hardness (at 25°C)	Needle Penetration (mm × 10) (100 g/25°C/5 sec)
Laurone	74	11.6
Palmitone	93	4.0
Stearone (m. 76°C)	96	2.1

The commercial ketones are unaffected by high temperatures, acid, alkali, or other strong agents. They are compatible with high-melting vegetable waxes, hydrocarbon waxes, triglycerides, and long-chain fatty acids.

Commercial Stearones. The specifications for commercial stearone vary considerably with the source of the material from which the stearone is derived, for example, (a) stearone produced from vacuum-distilled stearic acid; (b) stearone from triple-pressed stearic acid; and (c) stearone from solvent extracted stearic acid. Stearone (a) has a melting point of 80–85°C, specific gravity (d^{25}) 0.983, refractive index (n^{D}) 1.5164, acid value 4, saponification number 10, iodine number 6, ash 0.05 per cent, moisture 0.5 per cent.

In the cold the stearones are almost insoluble in polar solvents. There is a pronounced increase in solubility with an advance in temperature; e.g., 100 g of ethyl acetate dissolves 0.25 g of stearone (m. 75°C) at 30°C, 29 g at 60°C, and 120 g at 80°C. Stearones of high melting point are appreciably less soluble than those of low melting point as is shown in the table given below. Stearones of high melting point are only sparingly soluble in the cold in nonpolar solvents; those of low melting point are quite soluble. All stearones are very soluble in hot nonpolar solvents. Table 70 gives a comparison of the solubility of laurone (m. 67°C), palmitone (m. 76.5°C), and stearone (m. 80°C) in both polar and nonpolar solvents.

TABLE 70. SOLUBILITY OF COMMERCIAL KETONES IN VARIOUS SOLVENTS*

(Grams per 100 grams solvent)

	Ethanol (95%)	Ethyl Acetate	Acetone	Benzene	Cyclohexane
At 30°C					
Laurone	0.6	2.2	1.1	20.3	12.7
Palmitone	—	<0.1	0.1	1.7	1.4
Stearone	—	—	0.1	0.6	0.5
At 50°C					
Laurone	6	45.4	144	142	118
Palmitone	0.2	2.5	1.0	27.7	20
Stearone	0.1	0.1	0.4	12.7	9.3

* From Bulletin No. G-1, Armour Chemical Division.

When stearone is incorporated in paraffin wax (128/130°F AMP) it tends to elevate the melting point beyond the values given by a straight-line curve.

Per Cent Stearone (a)	Melting Point (°C)
0	53.6
10	57
20	60.5
33.3	65
50	70
75	74.5
100	78.5

Emery Industries, Inc. markets a stearone (m. 74–76.5°C) which is a light colored crystalline product, somewhat unctuous, wax-like, and free from odor and taste, under the designation "Emery C-846-R Stearone." It is derived from a mixture of stearic and palmitic acids and about one per cent of oleic acid. It is claimed to have the advantage over pure stearone of being tougher and harder, and does not contract on solidification. It has a flash point of 265°C (510°F), fire point 296°C (565°F), and is of good thermal stability until 300°C is reached. It has an unusual degree of chemical stability; concentrated HCl or dilute NaOH solutions have no apparent effect on it at normal temperatures.

Stearone (m. 80°C) of the Armour Chemical Division is prepared from commercial stearic acid ("Neo-Fat 18-61"), whose approximate composition is stearic 75, palmitic 22, and oleic acid 3 per cent. It has a ketone content of 92, hydrocarbons (C_{16} and C_{18}) 5, and free fatty acid (as stearic) content of 3 per cent.

Commercial stearones may be obtained in flake form, packaged in 50-lb multiwalled bags.

Commercial Laurone. Laurone is produced by Armour Chemical Division from lauric acid ("Neo-Fat 12") the approximate composition of which is caprylic 1.0 per cent, lauric 95 per cent, and myristic acid 4.0 per cent. The chemical and physical properties are as follows: melting point 67°C, color (NPA) 2, free fatty acid 0.6 per cent, per cent ketone 95.0, per cent hydrocarbon 4.4. It is a soft crystalline material having a faint odor characteristic of coconut fatty acids. The ground product is light cream in color. It is of a low order of solubility in both polar and nonpolar solvents in the cold. It is quite soluble in hot cyclohexane and in hot benzene. It is sparingly soluble in methanol, or in ethanol (95 per cent) hot or cold.

Commercial Palmitone. Palmitone is produced by Armour Chemical Division from palmitic acid ("Neo-Fat 16") the approximate composition of which is palmitic 90 per cent, stearic acid 6 per cent, and oleic acid 4 per cent. The chemical and physical properties are as follows: melting point 76.5°C, color (NPA) 2, free fatty acid 2.2 per cent, per cent ketone 94.6, per cent hydrocarbon 3.2. It is a fairly hard waxy material having practically no odor. It is of a low order of solubility in both polar and nonpolar solvents in the cold. It is quite soluble in hot cyclohexane and in hot benzene. It is almost insoluble in polar solvents hot or cold.

Uses of Commercial Ketones. Stearone is used in blends of synthetic rubber, such as Hycar, with polyvinyl chloride type resins. It functions as a lubricant in the calendering operation. It can be used as a water-resisting component in compounds used for the impregnation of leather and textile fabric gaskets. It is of value as a component in gasket impregnating compositions that must be both chemically and heat resistant. Stearone has

been successfully employed as a mold-release agent in the plastics industry. When made into a composition candle with paraffin wax it burns with a yellow flame.

The aliphatic ketones are of value in paste polishes, since they have good solvent retention power. In shoe pastes stearone or palmitone will produce gloss under high applied pressure, but neither produces the high gloss of laurone. Stearone with a large percentage of palmitone contracts less on solidification than with a low palmitone content.

Stearone is readily dispersed in soft water by the triethanolamine soap of stearic acid to form milky opaque emulsions. Stearone is used as a cylinder tallow. Admixed with petroleum waxes it is of considerable value in the electrical industry. The aliphatic ketones are considered nontoxic. They are compatible with beeswax, cetyl alcohol, hydrogenated castor oil, spermaceti, etc. used in the cosmetic industry.

The chemical reduction of stearone yields high melting alcohols. Stearone can be halogenated and replacement of halogens with solubilizing groups produces surface-active products. Chlorinated stearone when polymerized can be used as a pour point depressant of viscous lube oils. The hydrogenation of stearone in the presence of ammonia or primary amines yields high molecular weight amines of value in the textile industry.

Waxlike Hydroxy Ketones

Tressler and Schade[55] found that unsaturated ketones such as *oleone* when treated with concentrated sulfuric acid are converted into ethereal sulfates which can be hydrolyzed to form *hydroxy ketones*. These hydroxy ketones may be used as substitutes for Chinese insect wax in polishes, etc.

Alkyl Cyclic Ketones

Ralston and Christensen (Armour and Company)[47] found that stearyl, myristyl, lauryl, and other fatty acid chlorides will react with diphenyl ether or substituted diphenyl ethers to produce waxy solids. These high molecular weight alkyl-aryl ketones have the general formula RCOR′ in which R is a phenoxy radical, and R′ the alkyl radical of the fatty acid. Wax products may also be produced where R is a diphenyl radical, e.g., by reacting stearyl chloride with biphenyl. In a similar manner fatty acid chlorides may be reacted, employing the Friedel-Crafts reaction or Grignard synthesis, where R is furane, $(CH{:}CH)_2O$. These mixed furyl alkyl ketones are for the most part waxy solids.

Furyl heptadecyl ketone melts at 52.5–54.0°C, *methylfuryl heptadecyl ketone* at 68–69°C, *dibenzofuryl heptadecyl ketone* at 83–84°C, and corresponding *hendecyl* compound at 74–75°C. *Phenoxyphenyl heptadecyl* ketone melts at

68°C. *Diphenyl heptadecyl ketone* melts at 108–109°C, the corresponding *tridecyl* and *hendecyl* compounds at 102–103°C and 97–98°C respectively. The alkyl cyclic ketone waxes are suitable for electric insulation, in waxing and polishing compositions, and as additives of lubricating oils.

(9) SYNTHETIC ESTERS OF THE NATURAL WAX TYPE

Synthetic Wax Esters

Higher fatty acids may be reacted upon by higher fatty alcohols to form esters of the type found in natural waxes. The formation of such esters is facilitated by passing CO_2 through the molten mixture at an elevated temperature for a prescribed period of time. Belluci[7] obtained a high yield (95%) of *cetyl stearate* by passing a slow current of CO_2 through a mixture of equimolar amounts of stearic acid and cetyl alcohol at atmospheric pressure, with the reaction beginning at 220°C and advancing the temperature to 270°C in the course of two hours.

Waxlike esters may be produced by hydrogenating vegetable oils (glycerides) under high temperature and pressure with a copper-chromium-oxygen catalyzer to which has been added aluminum oxide or zinc oxide to greatly accelerate the formation of esters. The wax ester produced from soybean oil, according to Sinozaki and Adati[82], is more readily soluble in alcohol and somewhat less soluble in turpentine than beeswax. The melting point of the ester and its viscosity in turpentine solution is like that of beeswax, making it possible to use such a wax as a replacement wax for some purposes.

Waxlike esters were prepared by Grün and co-workers[81] by allowing the chloride of a fatty acid to react in slight excess with the fatty alcohol on a water bath while passing a stream of CO_2 through the reactants. After the free HCl ceased to be evolved the acid was neutralized with alcoholic KOH and the ester and fatty acids salt separated by petrolic ether and alcohol 1:1. To separate the unesterified wax alcohol the reaction product was extracted with hot ethanol in which the esters are insoluble. The esters were then crystallized from various solvents to a constant melting point. The yield was 90 to 95 per cent.

(10) WAXLIKE FATTY ACID AMIDES AND AMIDE DERIVATIVES BOTH ALIPHATIC AND AROMATIC

Long-Chain Fatty Amides

A primary amide may be described as an organic acid derivative in which the (OH) group has been replaced by an amine (NH_2) group, forming a substantially neutral chemical called an amide ($RCONH_2$). When R is a

long chain derived from the higher fatty acids the amide is a waxlike material. Such waxy amides appear to have been first prepared commercially by the Chemische Werke Hansa, Hemelingen, Germany, in 1906 by the simple well-known reaction:

$$RCOOH + NH_3 \rightarrow RCONH_2 + H_2O$$

The method consisted of melting down the fatty acid, e.g., stearic acid, in a closed vessel, and while heating the melt, passing gaseous ammonia through the mass under a carefully regulated pressure[16]. Kösters and Otteman[40] of Bremen improved upon the process by a system of continuous circulation of the NH_3 gas, withdrawing the water and ammonia during the reaction and returning the ammonia in a dried form to the autoclave.

Stearamide is a hard waxlike substance which melts at 109°C, boils at 251°C at 12 mm pressure, has a specific gravity (d^{15}) of 0.800, and a molecular weight of 283.3. It is insoluble in alcohol; it is also insoluble in other organic solvents, but quite soluble when such solvents are heated. It is chemically inert, and decomposes at above 190°C. Stearamide forms a stable emulsion with water which is neither acidic nor alkaline. Stearamide may be prepared according to the Bruson process (1935), by heating stearic acid sufficiently high (suitably 180–250°C) to split out water and cyanuric acid, and then recovering the amide by vacuum distillation.

Palmitamide, $C_{15}H_{31}CONH_2$, is a waxy solid similar to stearamide and has a trifle lower melting point. It is a component part of commercial grades of stearamide. *Arachidamide*, $C_{19}H_{39}CONH_2$, may be prepared in a similar manner to stearamide, starting out with arachidic acid. It melts at 109°C. The *N*-hydroxy amides of *cis*-11-eicosenoic and *trans*-11-eicosenoic acids melt at 79–80°C, and 93–94°C respectively. *Cis*-11-eicosenoic acid is obtainable from jojoba seed.

The longer the carbon chain of the amide the less is the solubility. However, they are all more or less soluble in warm ketones, esters, turpentine, mineral spirits, fats and fatty acids. The higher the molecular weight of the solvent the more amide it will hold in solution.

"Armids"

Commercial fatty acid amides go under trade designations, such as "Armid HT," a product of the Armour Chemical Division. According to the producer it has the following amide composition: palmitamide 22 per cent, stearamide 75 per cent, and oleamide (9-octadeceneamide) 3 per cent. "Armid HT" is a fairly hard, waxlike material, light tan in color, and possesses a compact crystal structure. It has a solidification point of 98°C, specific gravity (d^{25}) about 0.960, flash point 225°, and fire point 250°C. It is compatible with synthetic and natural waxes. The producer gives the

cloud points (°C) for the blends of "Armid HT" with other waxes as follows:

Wax	Per Cent of "Armid HT"			
	0	10	50	90
Paraffin	51	90	93	97
Carnauba	83	87	94	97
Stearic Acid	66	63.5	76	95
Ceresin	64	94	94	93
Ozokerite	67	93	95	97
Spermaceti	45	84	93	97
Beeswax	63	77	94	97
"Armid HT"	98			

Mixtures of "Armid HT" and rosin produce materials that vary from brittle waxes, through noncrystalline hard waxes, to high mellowing waxes. The addition of "Armid HT" to rosin markedly lowers the viscosity of the melt. Beeswax is simulated by the following formulation: WW Rosin 60, "Armid HT" 30, and mineral oil 10 parts.

The solubility of "Armid HT" in 100 ml of ethanol is 0.25 g at 10°C, 0.825 at 30°C, and 30 g at 65°C. In general its solubility in organic solvents, polar and nonpolar, is less than 1.3 g per 100 ml of solvent at 30°C.

"Armid C" is composed chiefly of amides of 12 and 14 carbon chain length, namely lauramide and myristamide. It is derived from coco fatty acids and has a mild odor common to these acids. It is a hard, pale material that is nontacky, waxlike in nature, and can be flaked like "Armid HT" or "Armid 18." "Armid C" has a solidification point of 85°C, specific gravity (d^{25}) 0.890, flash point 174°, and fire point 185°C. "Armid 18" is essentially stearamide. In composition it consists of 90 per cent octadecanamide, 6 per cent hexadecanamide, and 4 per cent 9-octadecenamide. It has a melting point of 104°C minimum. "Armid O" is essentially oleamide, 9-octadecenamide. It is a soft waxlike material that becomes ductile and smooth when worked between the fingers. "Armid O" is light in color, and has a solidification point of 68°C.

The "Armids" act as mutual solvents for waxes and plastics. They are used to the extent of 2 to 5 per cent as antiblock or antitack agents in plasticized synthetic resin formulations, and hence are of value in hot melt compounds used for coating strip or sheet material, such as foils. The synthetic resins may be vinyls, ethylcellulose, polyethylene, and methacrylates. Fluid coatings and plastics can be made with the "Armids" by employing straight petroleum solvents, or with the addition of butyl alcohol. In the making of composition for dental use, a preferred light color may be maintained by melting the composition under a blanket of inert gas, such as nitrogen or carbon dioxide.

An important use of "Armid T" is as an agent for blending ethyl cellu-

lose with wax; a little diphenylamine is said to prevent heat discoloration of the ethyl cellulose. Other uses for long-chain aliphatic amides are as a dye solvent in carbon paper manufacture, for candle dipping, for polishes, and for textile softening and sizing emulsions. Amides of any kind must not be heated beyond 170°C, nor boiled with acid or alkali, since they then undergo decomposition. Thermally unstable quaternary ammonium salts are prepared from the reaction of formaldehyde and stearamide, which when applied to fabrics from aqueous solutions and decomposed under heat leave an insoluble, durable, water-repellent residue within the fabric. Likewise the reaction product may be combined with thermosetting resins to produce durable water-repellent effects; some of these thermally unstable compounds are covered by patents.

Many synthetic resins can be made compatible with paraffin or microcrystalline waxes by using "Armids" as mutual solvents. "Armids" may be used as effective anti-offset, anti-scratch agents in printing inks. Unlike most of such agents they allow overprinting by another color.

An outstanding characteristic of "Armid O" is that it will promote solubility of both alcohol- and oil-soluble dyes that are used in conjunction with hydrocarbon waxes. Eight grams of "Armid O" will solubilize 2 g of crystal violet (extra pure KPN) or methyl violet S concentrate. Two grams of "Armid O" will solubilize 8 g of methyl violet base. "Armid O" will promote more effective solubilizing of methyl violet base when used in a predominantly hydrocarbon formulation such as pencil and typewriter coatings.

Aliphatic Amide Derivatives

When aliphatic amides of the long carbon chain fatty acids are reacted with an acid chloride, corresponding *acyl-substituted amides* form. The reaction is of the following order:

$$RCNH_2 + R'COCl \rightarrow RCNHCR' + HCl$$

In the presence of catalytic amounts of a strong acid, reaction with formaldehyde results in the formation of *methylenebisamides.*

$$2RCNH_2 + CH_2O \xrightarrow{\text{acid catalyst}} R{-}C{-}NH{-}CH_2{-}HN{-}C{-}R + H_2O$$

The waxes obtained are very hard and show fractures similar to carnauba wax. In their preparation Stegemyer[54] used a commercial stearic acid (45% stearic, 55% palmitic acid), and a ratio of formaldehyde to stearamide of 6:100. He states that ratios of 4–12 to 100 can also be used. The formalde-

hyde (i.e., paraformaldehyde) is added to the melted stearamide in a still which will allow the escape of the water formed but does not permit access of air. The heat is carefully applied so as to cause a slow evolution of HCHO from the paraformaldehyde, and is later slowly increased and maintained at 100–130°C for one hour; whence it is raised fairly rapidly to 160–170°C and maintained at this temperature for 3 hours or until the mix has a melting point of over 120°C. The resultant product is cooled to 130–140°C and passed into molds or a flaker. It has a durometer hardness of 68, and a melting point of 120–130°C; it is soluble in hot benzin, turpentine, and solvent naphtha, which solutions set to a smooth paste on cooling. They are unaffected by boiling water, are weather resistant, and can be dispersed in water to form stable emulsions.

"Armowax"

A synthetic wax which is essentially *N,N'*-methylenebis-stearamide is marketed under the name of "Armowax" by Armour and Company. Its melting point and other properties are not unlike those of "*Acrawax C.*" In its preparation two moles of stearamide are reacted with one mole of formaldehyde (in form of paraformaldehyde) in the presence of an acid catalyst. The reactor vessel is similar to that used for general esterification purposes.

"Armowax" is light tan in color, and of a mild odor. It has an acid value of about 12, and a saponification number of about 17. It melts at 132–135°C (270–275°F), has a penetration (200 g/5 sec/25°C) of 0.22 mm, specific heat 0.532 @ 60°C, flash point 250°C, and fire point 258°C. It yields 0.03 per cent ash, and is resistant to acids and alkalis. "Armowax" is compatible with carnauba, beeswax, ceresin, and ozokerite in all proportions; it is compatible with paraffine mixed 1:1, but only partially compatible when mixed 1:10. "Armowax" is soluble in mineral oils, naphthas, turpentine, butanol, methyl or butyl cellosolve, toluene, and xylene, when these solvents are hot. It is insoluble in benzene, ethyl alcohol, ethyl acetate, carbon tetrachloride, petrolic ether, acetone, and ethylene dichloride.

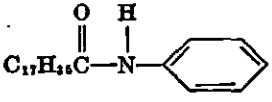
In blending "Armowax" with paraffin wax it is best melted first, not too highly, and the paraffine added slowly. The paraffin wax when in excess becomes the solvent and the "Armowax" the solute, depressing the crystallization of the paraffin on congealing. Small quantities such as 5 per cent greatly elevate the melting point of both paraffin and beeswax, whereas the effect on stearic acid is negligible. When "Armowax" is melted and dissolved in polar and nonpolar solvents it has a tendency to gel on cooling. "Armowax" has been found useful as an ingredient in shoe pastes and floor polishes, for sound records, protective coatings, water dispersed adhesives, carbon papers, etc. "Armowax" is of value as a lubricant in powder metallurgy.

It is mixed with the metallic powder which is to be molded, and the molded metal removed from the hydraulic press is sintered to form the casting; in some instances the sintered metal may be swaged and drawn.

"*Armowax*" should not be confused with "Armorwax," a trade name given to a new series of petroleum waxes of the Pennotex Oil Corporation, New York, the uses of which include paste and liquid solvent floor waxes.

Stearanilide

Stearanilide (m. 83–84°C) is a condensation product of aniline and stearic acid. It has the structural formula



Commercial stearanilide (e.g., "Emery A-805-R Stearanilide") is a hard, relatively high melting, wax-like material. It has the following chemical and physical characteristics: melting point 80–82°C, hardness ("Shore Durometer B") 60–70, color light tan, free fatty acid 1–2 per cent, flash point 249°C (480°F), fire point 279°C (535°F). Stearanilide is slightly crystalline, odorless, and shrinks markedly on solidification. It is soluble in most solvents at room temperature, but readily soluble in many hot solvents. In solvents such as varnolene stearanilide does not form macro-crystals at its precipitation point (60°C), but yields a gel; smooth, soft white pastes result at high solids concentration. It has excellent binding characteristics since it shows little evidence of solvent release. Stearanilide is compatible with many waxes, including paraffin, microcrystalline, carnauba, and beeswax, and with synthetic waxes such as polyethylene wax.

It may be used as a natural wax substitute or extender in paste or cream-type wax polishes. The hardness of the wax film can be improved by the use of small percentages of "F-T Wax." Its use has been suggested for carbon paper. Many chemical derivatives for use in textile and other industries can be made through substitution in the benzine ring or of the amino hydrogen.

Cetylacetamide Wax

The condensation product of two mols of an acetamide of a long-chain aliphatic group and one mol of formaldehyde yield an amide wax of a composition which will form a heat-reversible gel. Cetylacetamide wax (N:N'-methylene-bis-cetylacetamide) is prepared from 2 mols of cetylacetamide and 1 mol of formaldehyde (paraform) with the aid of an acid catalyst. The wax has a melting point of 137–139°C.

Synthetic waxes of the cetylacetamide type exhibit good resistance to

moisture and to oxidation, and have good dielectric resistance. When 90 parts of asphalt are mixed with 5 parts of butyl methacrylate resin and 5 parts of the wax, the resulting properties of the blend reveal a viscosity, softening point, cold flow, etc. suited for potting and sealing compounds used as impregnating agents for coils and other electrical equipment. [Cf. Lowden, W. P., and Pitman, N. J. (Radio Corporation of America), U. S. Patent 2,486,487 (1949)].

(11) WAXLIKE IMIDE CONDENSATION PRODUCTS

"Acrawaxes"

"Acrawaxes" are complex nitrogen derivatives of the higher fatty acids. These synthetic waxes are produced in several grades by the Glyco Products Company, New York. Grades known as "A," "B," and "C" melt at 95–97°C, 86–90°C, and 140–143°C respectively. The composition of "Acrawaxes" has not been disclosed, but they have chemical and physical characteristics not unlike those of products prepared by the condensation of a cyclic imide and a fatty acid, such as stearic acid and/or its homologs. "Acrawax C" is a wax of unusually high melting point; it is light tan in color, very hard, and has a high luster.

A specimen of "Acrawax C" had a melting point of 137–140°C (278.6–284°F); flash point 285°C (open cup); specific gravity of 0.975 at 25/25°C, and of 0.831 at 141/25°C in molten state; moisture absorption (48 hr at 100% R.H.) 0.6 per cent at 35.5°C; and dielectric resistance 428 volts per million. "Acrawaxes" are insoluble in water but soluble in hot hydrocarbon solvents. "Acrawax C" is available in bead form.

"Acrawax C" is insoluble in alcohol, and when dissolved in turpentine or in *ortho*-dichlorbenzene produces a gel on cooling. This wax has been listed as compatible (ratio 1:1) with asphalt, candelilla wax, carnauba wax, microcrystalline wax, paraffine, stearic acid, and several resins. Important applications are: antitack, antiblock, and antistatic agents in resins and in synthetic rubber; lubricants for metals; plastics and synthetic rubber; electrical sealants and insulation coatings; adhesives—hot melts and water dispersions; flatting agents; dental waxes; electroplating "stop off" waxes; textile coatings; asphalt blends; paints, varnishes, and lacquers[49].

Imide Condensation Derivatives from Secondary Amines

A waxlike product of the Resinous Products and Chemical Company, according to the specifications set forth in their German letters patent 641,865 (1937), is obtainable by heating formaldehyde with a strongly basic secondary amine of the general formula R·NH·R′, in which R and R′ represent alkyl and alkylene short-chain groups, and with a primary amide of more than 8 carbon atoms. The primary amide may be that of an ali-

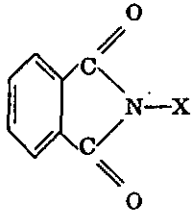
phatic, hydroaromatic, or naphthenic carboxylic acid. An inert volatile solvent or a basic catalyst such as trialkylamine, or an alkaline mineral substance may also be present. In an example, *stearamide* is heated with dioxane, commercial aqueous dimethylene solution (containing 41% dimethylamine, 0.4% monomethylamine, and 38% trimethylamine), and a 30% aqueous formaldehyde solution, to give a waxlike product.

The addition of up to 3 per cent by weight of a stearic acid amide of ethylene diamine to a composition containing a vinyl copolymer and a plasticizer is effective in preventing blocking of plasticized films [Duggan, W., and Stambaugh, R. P., U. S. Patent 2,464,855 (1949)].

A wax produced from stearic acid and ethylene diamine has the composition *N:N'-distearoyl ethylene diamine*. It melts at 137.5–143.5°C (280–290°F) and has an acid value 10 max., flash 545°F, fire point 580°F, and dielectric strength 400 v/ml. Its color is tannish white. It is of value as an antiblocking, waterproofing, electrical insulating, and mold release agent. It is used in asphalt compositions for pipe wrap asphalts, and in electrical potting and dipping wax blends; also to increase softening point and inhibit cold flow properties. It is a mutual solvent for polyamide resin and paraffin wax for heat-sealing wax papers. A lower melting grade (m. 240°F) is favored for this purpose. It is claimed that it stops breathing of waxed paper and assists the heat sealing and antiblocking properties [Carlisle Chemical Works].

Phthalimides

High molecular weight phthalimides of the general formula



wherein X is a straight chain hydrocarbon radical having six or more carbon atoms have been found by Pool and Harwood[45] to be very waxlike. They give an extremely high luster when polished, and when dissolved in an appropriate solvent make an excellent waxing and polishing composition.

The phthalimides can be prepared by heating one mole of phthalic anhydride with one mole of a primary aliphatic amine until the evolution of water ceases. For example, 185 grams of dodecylamine (X 12) and 148 grams of phthalic anhydride are mixed in an open flask and then heated to 165°C for a period of four hours, at the end of which time the evolution of

water ceases. The product, *N*-dodecyl phthalimide, is poured into molds and allowed to solidify. It is a medium hard, light-colored wax, which melts at 65–67°C. *N*-tetradecyl, *N*-hexadecyl, and *N*-octadecyl phthalimides have melting points of 70–72, 75–77, and 80–81°C respectively. However, a commercial phthalimide which is a mixture of the three phthalimides had a melting point of 55–57°C.

N-octadecyl phthalimide in its pure form is reported to have a melting point of 96.5°C. The commercial form contains about 0.8 per cent of free phthalic acid, 94 per cent of *N*-octadecyl phthalimide, and 0.5 per cent moisture, and has a saponification number of 141. Phthalimides are hydrolysed easily by strong alkalies.

Ericks[24] prepared a waxlike product, suitable for use in coating compositions, adhesives, floor polishes, artificial fibers, etc., by heating *N*-ethylol or *N*,*N'*-diethylol guanidine acetate (or hydrochloride) with phthalic anhydride.

Sometimes the phthalimide waxes are used with carnauba wax in a 50:50 ratio, and the mixture emulsified for waxing and polishing compositions. In other instances the phthalimide waxes are mixed with the solvent to make a polishing paste. Their utilization has been suggested as a raw material in carbon paper coating manufacture.

(12) REACTION PRODUCTS OF A MONOETHENOID HYDROCARBON AND A SILICON HALIDE

Silicon Wax

Waxlike polymers, according to Scott[50], can be prepared from a polymerizable aliphatic monoölefinic hydrocarbon (e.g., ethylene) by reacting it with a silicon halide (e.g., silicon teroachloride). The reaction is carried out at high pressure (600–1000 atm.) at 75–300°C, with or without an inert solvent (e.g., cyclohexane). A polymerization catalyst which is ineffective in the Friedel-Crafts reaction is used. Suitable catalysts are diethyl peroxide, or a combination of potassium perchlorate and manganese dioxide. With ethylene and silicon chloride as the reactants, a waxlike polymer of an optimum molecular weight of 4000 and an optimum melting point of 110°C can be obtained which is useful for polishes, paper coatings, and the like. Lower polymers are greaselike and useful as modifying agents of lube oil. (Also see Silicone-Wax Compositions, p. 518.)

(13) POLYETHYLENE POLYOL FATTY ACID ESTERS AND DERIVATIVES

Polyethylene Glycol Esters

The polyethylene glycols ("Carbowaxes") can be reacted with fatty acids, either unsaturated (e.g., oleic acid) or saturated (e.g., stearic acid)

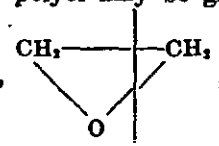
to form a series of useful liquids and solids. A few of the commercial polyethylene glycol esters are waxy solids. They include "Carbowax 4000 (Mono) Laurate" (m. 50–60°C), "Polyethylene Glycol 600 (Mono) (Di) Stearate" (m. 24–26°C), and "Carbowax 4000 (Mono) Stearate" (m. 54–57°C). These are products of Carbide and Carbon Chemicals Co.

In making polyethylene polyol esters, the polyhydric alcohol used may be varied from the two carbon atom dihydric alcohol, ethylene glycol, or the trihydric alcohol, glycerol, to one of a molecular weight of about 6000 such as "Carbowax 6000," a polyethoxy dihydric alcohol (polyethylene glycol). The fatty acids range from C_{12} to C_{18}. Reacting one mol of fatty acid with one mol of polyhydric alcohol will give a monoester which is generally hydrophilic. The diesters, lipophilic, are obtained by reacting two mols of fatty acid with one of polyhydric alcohol.

The principal uses to which the polyglycol fatty acid esters are put depend on their surface activity and emulsifying action. A number are good wetting and penetrating agents and detergents. Some are plasticizers and lubricants for plastics, etc. "Carbowax 1000 (Mono) Stearate" is a yellow, waxy solid, which is soluble in hot water. It is an antigelling agent, i.e., 0.1 per cent based on the weight of the starch definitely retards "setting-up" of the starch solutions, keeping them fluid.

Waxy Polyol Ether-Esters

Waxlike compounds are synthesized by treating a mixture of a polyol (e.g., *sorbitol*) and water with an olefine oxide (e.g., *ethylene oxide*), and then esterifying the reaction product with *palmitic* or *stearic acid*. Brown[13] states that the reaction of the polyol with olefine oxide takes place in a pressure vessel, stirring in presence of a catalyst like boric acid, sodium oleate, sodium methylate, sodium phosphate, etc. The esterification is performed in closed vessels at 150–280°C; the water is removed by distillation. The end products are tough, long-fibered, inexpensive waxes, easy to melt, and of good light and chemical stability; they show cohesiveness, lubricity, plasticity, and lack of brittleness. Waxy polyol ether-esters are soluble in hydrocarbons at low temperature and are readily dispersible in warm water. They are useful as waxes and lubricants for cosmetics, yarn sizes, polishes, and wax-base protecting compositions.

In polyol ether-esters the polyol may be glycerol, sorbitol, mannitol, glucose, etc. Ethylene oxide,  , is preferred to propylene oxide because it gives a higher-titer wax. In the pressure vessel the addition of excess water produces brittle waxes, and too high a temperature re-

sults in dark products which may be decolorized with carbon black, activated earth, hydrogen peroxide, or benzoyl peroxide. Derivatives of natural waxes can be made by reacting on the acid constituents of such waxes, e.g., *polyoxyethylene sorbitol beeswax derivative*, and *polyoxyethylene sorbitol lanolin derivative*. These derivatives and other polyol ether-ester waxes are manufactured by the Atlas Powder Company.

Polyoxyethylene sorbitan monostearate is commercially known as "Tween 61," whereas "Span 62" is *sorbitan monostearate*. These hydrophylic and lyphophilic agents are extensively used in the textile industry.

(14) MISCELLANEOUS SYNTHETIC WAXES—UNCLASSIFIED

Aerosol Spray Wax

Aerosol dispensers are containers with a finger-tip push button mechanism in the closure which enables the user to spray the contents on the surface to be waxed, saving trouble and the inconvenience of applying wax with a cloth. The aerosol spray principle is extensively used for spraying deodorants, insect killer, etc. Aerosol dispensers are now used for household wax, automobile spray wax, etc.

Unfortunately, "Aerosol" is also the trade name given by the American Cyanamid Company to the diakyl salts of sulfosuccinic acid, that characteristically are *wetting agents*, e.g., "Aerosol OT" is *dioctyl sodium sulfosuccinate*. It resembles white slack wax in appearance and consistency, except that it is marketed in extruded pellet form. "Aerosol OT" has a molecular weight of 444; has a slightly camphoraceous odor and taste; is somewhat hygroscopic; is dispersible in warm water; and is soluble in most polar and nonpolar solvents, in warm oils, fats, and resins when heated to 75°C. It is not directly miscible with hydrocarbon waxes but mixes well with beeswax and most of the vegetable waxes. "Aerosol OT" may be coated on polyethylene transparent wrappings to prevent fogging. It is used as an emulsifier for insecticidal sprays.

"Aerosol MA" is chemically known as *dihexyl sodium sulfosuccinate*; it is less soluble than the dioctyl compound in organic liquids, but dissolves readily in hot water. Both act as good wetting agents in formulations of floor waxes, in washing photographic prints, and in the dental laboratory for wetting wax investments in order to prevent the formation of bubbles with consequent imperfections during the casting of plaster.

"Bohrer's Wax"

"Bohrer's Wax" is a condensation product of monoamylamines and tetrachlorophthalic anhydride. It is on the borderline of a class of waxes which comprise the halogenated paraffin and chloroparaffin cyclic condensation waxes; waxes that are flame resistant or fire retardant because of

their halogen content. "Bohrer's Wax" is prepared by reacting under heat equimolar quantities of a mixture of monoamylamines (95% distilling at 100°C) and tetrachlorophthalic anhydride until an acid number of 35 is obtained. Addition of anilin raises the melting point of the product.

According to the Bohrer patent[10], 550 g of the amines is added to 1750 g of the anhydride which has been dispersed in 1750 g of a suitable hydrocarbon solvent such as "Solvesso #1" and the whole stirred and refluxed for 2 hours. Upon removal of the volatile matter by distillation there remains a wax which melts at 128–130°C and has an acid number of 32. If 10 per cent of the monoamylamines is replaced by anilin, the melting point of the wax is of the order of 144–148°C, and acid number 25. The waxes are of value as protective coatings to prevent corrosion and decay. They are also of value as dielectrics. "Bohrer's Wax" is considered nontoxic.

"Duroxon Waxes"

Under the designation of synthetic mineral waxes are offered not only "F-T Waxes," but more or less saponifiable waxes, known as "Duroxon Waxes" (Dura Commodities Corporation, New York). "Duroxon J-324" is a pale yellow wax, said to be based on the F-T process, which has a melting point of 212–218°F, acid value 5–15, saponification number 30–40, and penetration value (100 g/5 sec/77°F) of 2–4. It is readily emulsified in water, employing morpholine and oleic acid as saponifying agents. The wax is recommended for formulations of self-polishing water emulsions for use on flooring material, such as asphalt tile, linoleum, rubber tile, and the like. Carnauba wax may be used in conjunction with "Duroxon Wax" to improve the body and stability of the finished self-polishing waxes. "Duroxon Wax H-111" is a yellow hard wax described as being especially suited for shellac-compatible nonionic emulsions. "Duroxon E-321" is a special hard wax for liquid solvent type polishing formulations.

Oxygenated Hydrocarbons

Oxo Process. In the Oxo synthesis, olefins, carbon monoxide (CO), and hydrogen (H_2) are brought into contact in a first reaction zone with supported cobalt, nickel, or iron catalyst under conditions to produce oxygenated hydrocarbons. The effluent with entrained catalyst metal carbonyl is treated in a second zone in the presence of the same type of catalyst with hydrogen under conditions to decompose the carbonyl. The flow through the system is periodically reversed. The products from the first zone can be hydrogenated in the second zone, or in an additional third zone[30].

Preferably three stages are used, in which H_2 free from CO is introduced in the third stage and recycled there; a part of the recycling gas is led to the second stage, in which H_2 with some CO is recycled, and a part of this gas

is introduced into the first stage, together with CO, so that here a gas mixture containing 1 CO to 1 H is recycled. A temperature of about 150°C and 200 atmospheres pressure are employed in the first and second stages. The carbonyl compounds can be decomposed at 100 atmospheres pressure. The oxygenated products after distillation are hydrogenated in a manner that will convert aldehydes and ketones into the corresponding alcohols. Catalysts in the form of metallic soaps, such as cobalt stearate, nickel oleate, and iron linoleate, which can be dissolved readily in the olefin feed, have been employed.

Stationary beds of a solid nickel silicate have been proposed by Engel and Koome[21] for the refining of crude synthetic alcohols by catalytic vapor-phase hydrogenation.

The Blaw-Knox Company has developed a plant for Ruhrchemie A.-G. Germany, to produce the so-called "molecular" waxes by the Oxo process. Such waxes have a melting point of about 240°F or higher. A pilot plan has been completed, and a commercial plant destroyed in the war is being refurbished and redesigned [Chemical Week Report (Sept. 27, 1952)].

Polypentaerythritol Ester Complex

Waxlike products have been prepared by esterifying *pentaerythritol*, or *polypentaerythritol* with saturated fatty acids and maleic anhydride. According to Burrell and associates[15], the waxy products are compatible with all common natural waxes, are soluble in hydrocarbon solvent, and may be emulsified to form paste waxes, useful as coatings and polishes. An example of the preparation of these waxes is given by these investigators. Stearic acid 1000, pentaerythritol (85% mono- and 15% di-) 168, and calcium naphthenate 10 parts are heated in a blanket of CO_2 for 1¼ hours at 250°C. The mixture is cooled to 150°C, 58 parts of maleic anhydride are added, and the temperature is raised to 250°C for 4 hours. The product is a hard, light brown wax (m. 65.2°C). Mixing 50 parts of this wax with 25 parts of rosin gives a soft wax resembling beeswax in appearance, color, and odor; it has a melting point of 58.4°C. Fatty acids other than stearic may also be employed in the formulations.

Santowaxes

"Santowaxes," products of the Monsanto Chemical Company, St. Louis, Missouri, were formerly listed as waxes. They are cyclic hydrocarbons, and bear little resemblance to waxes. They have a terphenyl structure, i.e., *ortho-*, *meta-*, and *para*-diphenyl benzene, or mixtures of these or allied derivatives. They were marketed as O, M, P, and R (regular) "*Santowax*." In general, they are hard, of unpleasing odor, heavier than water, unstable in melting point, and stable to heat. The *ortho* (O) type is yellow, and solidi-

fies at 140°F; it takes a long time to harden. "Santowax M" is microcrystalline, and will become as hard as candelilla; it is very stable to heat, and has a melting point of 181–184°F. "Santowax P" is nearly white, crystalline, and very stable to heat; it has a very high melting point, and solidifies at 411–417°F. "Santowax R" is a yellow glaucous solid with a melting point range of 140–193°F. It was much lower priced than the purified isomers, and the only one extensively used. The uses for the "Santowaxes" have been described as rust-inhibitive coatings for steels, antifouling and fire-retardant resinous paints, coatings for paperboard, etc.

Waxes Produced from Fatty Acid Anhydrides

Waxes can be produced by heating anhydrous fatty acids, such as lauric anhydride (m. 42.1°C), myristic anhydride (m. 53.5°C), palmitic anhydride (m. 63.9°C), and stearic anhydride (m. 70.7°C), or mixtures of these anhydrides, in a thin layer over Raney nickel catalyst in a nitrogen atmosphere over a period of several days. For example, stearic acid anhydride, $(C_{18}H_{35}O)_2O$, when heated with Raney nickel for a prolonged period of time at 220°C or above yields a wax which is a mixture of *stearyl octadecanoate*, free *stearyl alcohol*, and *stearone*, with a considerable evolution of CO_2 from the reaction. The wax melts at about 60°C (140°F).

Bleyberg and Ulrich[9] in 1931 determined the melting points, densities, and refractive indices of several of the wax acid anhydrides:

Number of Carbons	M.P. (°C)	Density (d^{100})	Refractive Index (n_D^{100})
20	77.5–77.7	0.8225	1.4301
22	81.7–81.9	0.8206	1.4320
24	86.0–86.3	0.8196	1.4329
26	89.3–89.5	0.8188	1.4337
28	92.7–92.9	0.8183	1.4345
30	94.6–94.7	—	1.4552

Synthetic Waxes of Glyco Products Company

Included in the waxes listed by the Glyco Products Company other than the "Acrawax C" already described, are those in which the chemical compositions have not been fully disclosed, and which bear trade names as "Albacer," "Ceramid," "Flexo Wax C," "Glyco Wax S932," "Rezo Wax B," and "Stroba Wax."

"*Albacer*" is a very hard lustrous white wax which melts at 99–104°C. It is used as an additive to paraffine for wax-coated paper used in wrapping sticky candies. "*Ceramid*" is a hard, yellow wax, which melts at 79.5–80.5°C, and has a high flash point (260°C, open cup). It is readily soluble in cold solvents. "*Flexo Wax C*" is a noncrystalline hydrocarbon wax with high

adhesive properties. It melts at 64–70°C. Dissolved in turpentine and applied hot it is a good adhesive for tissue paper to aluminum. *"Glyco Wax S932"* is an edible waxlike ester which melts at 57–61°C, and has a flash point of 328°C. It is used in greaseproof coatings, and as a plasticizer for chewing gum. *"Rezo Wax B"* is a very hard, light brown wax which softens at 95°C and melts to a clear fluid at 110°C. It is used in molding phenol-formaldehyde compositions, and in paste polishes. *"Stroba Wax"* is a hard, tan wax, which melts at 98–102°C. It is useful in paints, varnishes, and lacquers; and as an ingredient in paste polishes. When blended with paraffine it gives increased luster and melting point to paraffined papers.

The output of synthetic waxes by Glyco Products Company is believed to be approximately 1.5 million pounds per year.

Wax Telomers

In a reaction mechanism of Hanford and Roland[25] called *telomerization*, *telogens*, such as dialkyl ethers free of olefinic unsaturation, are allowed to react with ethylene, a *taxogen*, under more than 200 atmospheres pressure at 50–250°C and with a peroxy catalyst to yield *telomers* which in this case are hard waxes resembling carnauba. Analysis of the telomers reveals *taxomon* units which consist of a plurality of taxogen molecules linked terminally to the fragments of the telogen. These investigators also produced telomers of monoölefins and halogenated carboxylic acids and their derivatives in a silver-lined pressure reactor, some of which have wax-like characteristics.

References

1. Anonymous, Mellon Institute, Pittsburgh, Pa., *Chem. Eng. News*, **18**, 2 (1940).
2. Aylsworth, J. W., U. S. Patents 914,222 and 914,223.
3. ——, U. S. Patent 1,111,289 (1914).
4. Barth, E. J., *Petroleum Refiner*, **25**, 124–125 (1946).
5. Bell, S. A., and Taub, A., *J. Am. Pharm. Assoc.*, **31**, 75–81 (1942).
6. *Ibid.*, **32**, 115–118 (1943).
7. Belluci, I., *Chem. Ztg.*, **35**, 669 (1911).
8. Benson, H. E., *et al.*, *Ind. Eng. Chem.*, **46**, 2278–2288 (1954).
9. Bleyberg, W., and Ulrich, H., *Ber.*, **64B**, 2504–2513 (1931).
10. Bohrer, G. J. (to General Electric Co.), U. S. Patent 2,443,888 (1948).
11. Bolley, *Ann.*, **106**, 230 (1858).
12. Bradley, T. F. (to American Cyanamid Co.), U. S. Patent 2,367,712 (1945).
13. Brown, K. B. (to Atlas Powder Co.), U. S. Patent 2,450,070 (1948).
14. Buckley, G. D., Ray, N. H., and Imperial Industries, Ltd., British Patent 669,771 (1951).
15. Burrell, H., *et al.*, U. S. Patent 2,427,255 (1947).
16. Chemische Werke Hansa, German Patent 189,477 (1906).
17. Davis, H. S., U. S. Patent 1,815,022 (1931).
18. Easterfield, T. H., and Taylor, C. M. (Victoria College, N. Z.), *Proc. Chem. Soc.*, **27**, 279 (1911), *J. Chem. Soc.*, **99**, 2298–2307 (1911).

19. "Economic Study of German Synthetic Waxes" (Steinle, J. V.), Office of Military Government for Germany (U. S.), PB-No. 11173, U. S. Dept. of Commerce Report, Washington, D. C. (1945).
20. E. I. du Pont de Nemours & Co., Inc., British Patent 399,848 (1933).
21. Engel, W. F., and Koome, J., U. S. Patent 2,525,354 (1950).
22. Engelhardt, R., German Patent 548,260 (1927), U. S. Patent 1,933,422 (1933), British Patent 324,774 (1929), French Patent 667,024 (1928).
23. Erchak, Jr., M. (to Allied Chemical and Dye Corp.), U. S. Patent 2,504,400 (1950).
24. Ericks, W. P. (to American Cyanamid Co.), U. S. Patent 2,298,473 (1942).
25. Fischer, H. O. L., and Koch, H., *Brennstoff-Chem.*, **13**, 428 (1932).
26. Friedman, A. H., U. S. Patent 2,500,533 (1950).
27. Frolich, P. K., U. S. Patent 2,322,012 (1943).
28. "German Montan-Wax Industry," Report by British Intelligence Objectives Subcommittee, London, 1945.
29. Girelli, A., and Siniramed, C., *Riv. combustibili*, **3**, 311–319 (1949), cf. *Chem. Abstracts*, **44**, 3244 (1950).
30. Green, S. J. (Canadian Industries, Ltd.), Canadian Patent 371,129 (1938).
31. Grün, A. D., Ulbrich, E., and Krczil, F., *Z. angew. Chem.*, **39**, 421–428 (1926).
32. Guyer, August, U. S. Patent 2,110,483 (1938).
33. Hall, E. E., *Ind. Chemist*, **9**, 58–60 (1933).
34. Hamai, S., *Bull. Chem. Soc. Japan*, **16**, 213–228 (1941), *J. Chem. Soc. Japan*, **62**, 516–518 (1941), cf. *Chem. Abstracts*, **37**, 4681 (1943).
35. Hanford, W. E., and Roland, J. R., U. S. Patents 2,457,229 (1948) and 2,507,568 (1950).
36. Heckel, H. (Hydrocarbon Synthesis Corp.), U. S. Patent 2,339,927 (1944).
37. Jahrstorfer, M., and Schwarte, G., German Patent 695,860 (1940).
38. ——, and ——, U. S. Patent 2,134,333 (1938).
39. Koch, H., and Ibing, G., *Petroleum Refiner*, **22**, 9 (1943) [translated from *Brennstoff-Chem.*, **16**, 141–148 (1935).]
40. Kösters, O. A. H., and Otteman, L., British Patent 6,731 (1907), U. S. Patent 915,680 (1909).
41. McClelland, C. P., and Bateman, R. L., *Chem. Eng. News*, **23**, 3, 247 (1945).
42. Normann, W., U. S. Patent 2,242,017 (1914).
43. Perrin, W., *et al.* (Imperial Chemical Industries, Ltd.), British Patent 497,643 (1938).
44. Petrov, A. D., *et al.*, *Compt. rend. acad. sci., U.S.S.R. N.S.*, **4**, 31–35 (1935).
45. Pool, W. O., and Harwood, J., U. S. Patent 2,225,392 (1941).
46. Pungs, W., and Jahrstorfer, M., German Patent 560,734 (1932).
47. Ralston, A. W., and Christensen, C. W., U. S. Patents 2,033,540, 2,033,541, and 2,033,542 (1936).
48. Reiff, O. K., U. S. Patent 2,191,499 (1940).
49. Sayre, J. W., and Marsel, C. J., *Chemical Week*, **71**, No. 13, 29–50 (1952).
50. Scott, S. L. (to E. I. du Pont de Nemours & Co., Inc.), U. S. Patent 2,497,181 (1946)
51. Shinozaki, and Kubo, H., *J. Agr. Chem. Soc. Japan*, **13**, 12–17, 18–22 (1937).
52. Sinozaki, Y., and Adati, S., *J. Agr. Chem. Soc. Japan*, **14**, 1135–1143 (1943).
53. Snell, F. D., and Guiteras, A. F., U. S. Patent 2,385,849 (1945).
54. Stegemyer, L. A. (to Emery Industries, Inc.), U. S. Patent 2,393,202 (1946).
55. Tressler, D. K., and Schade, C., U. S. Patent 1,941,639 (1934)
56. Zöllner, W., *Farben, Lacke, Anstrichstoffe*, **3**, 385–390 (1949).

7. Commercial Modified, Blended, and Compounded Waxes

Many of the waxes offered in commerce under trade names are blended or compounded waxes. Obviously it is possible to produce innumerable mixtures of waxes for use in the industries—far more than can be described. Hence, only an attempt will be made to classify and describe some of the important types of these waxes as are ordinarily obtainable in commerce. At the same time compounds prepared with wax as the principal ingredient will be discussed. Tabular information concerning the physical characteristics as they change by varying percentages of components will also be given for some of the compounded waxes, such as paraffin-carnauba wax blends, mixtures of hydrocarbon waxes with polyalkenes, etc. Modified waxes, blended waxes, and compounds of wax with nonwax materials can be grouped as follows:

(1) *Modified Waxes*

- (a) Hydrocarbon waxes modified by oxidation to make them saponifiable.
- (b) Natural waxes modified by distillation.
- (c) Natural ester type waxes, such as beeswax, altered by heating with or without a chemical agent.
- (d) Nonsaponifiable synthetic waxes modified to make them saponifiable, such as emulsifiable polyethylene.

(2) *Blended Waxes*

- (a) Mixtures of hydrocarbon waxes, such as commercial ceresins.
- (b) Blends of petroleum waxes with natural waxes.
- (c) Blends of hydrocarbon waxes with synthetic waxes, other than polyalkenes.
- (d) Blends of hydrocarbon waxes with polyalkenes.

(3) *Compounds of Wax with Nonwax Materials*

- (a) Waxes compounded with resins.
- (b) Waxes combined with resins and/or nonrubber elastomers
- (c) Waxes compounded with natural or synthetic rubbers.
- (d) Waxes compounded with cellulose ethers.

(4) *"Replacement" or Substitute Waxes*

(1) MODIFIED WAXES

Oxidized Hydrocarbon Waxes

The oxidized hydrocarbon waxes are an important class of the group of modified waxes. The outstanding hydrocarbon waxes modified by a chemical process of oxidation are petroleum waxes of the microcrystalline type. They are commonly referred to as OMC waxes, and exemplified by products of the Sun Chemical Corporation, Chanute, Kansas, known as "Cardis Waxes." In melting point the various grades of OMC waxes range from 180 to 200°F, with acid values from below 10 up to 30, and saponification numbers from below 40 up to 80 (see p. 528).

Vacuum-Distilled Waxes

Attempts have been made in the past to distil, at a pressure of 5 mm or less, crude mineral waxes, such as ozocerite, peat, and montan, to produce pure white commercial waxes for use in candles, etc., but only with a limited degree of economic success.

Vacuum-distilled beeswax, according to Humes[9], if prepared by distilling beeswax at a pressure of 0.001 to 0.1 mm and at a temperature depending on the pressure, e.g., 200–300°C at 0.01 mm, and 180–240°C at 0.1 mm. The product condensed at 95°C is characterized by a melting point of 55–65°C, acid value 40–65, ester value less than 30, and iodine number 5–10. It is white in color, practically odorless, and greatly enhances the retention of emulsified water in creams, etc.

Modified Ester Type Waxes

The properties of natural ester type waxes, such as beeswax, carnauba wax, spermaceti, candelilla wax, etc., are modified by heating with reagents of various kinds. According to Auer[3], beeswax (m. 64°C, acid value 20, saponification number 93) when heated with 5 per cent of sodium bisulfite ($NaHSO_3$) for 5 hours at 300°C under a blanket of carbon dioxide (CO_2) gas produced a modified wax of 137°C melting point, acid value 1.95, and saponification number 96.4. Such products are said to be useful ingredients for polishes, dental waxes, sealing waxes, and ski waxes, and are employed as impregnants for carbon paper and typewriter ribbon.

A tan-colored refined wax, basically montan wax but of lower free acid and ester contents than deresinified montan wax, is imported from Europe and marketed under the name of *"Durmont 500"* (Dura Commodities Corporation, New York). It has a melting point of 88–91°C, acid value of 3–5, and saponification number of 36–40. It is a hard, high-gloss wax, of excellent solvent binding capacity, comparable with carnauba wax in that

respect. "*Durmont 500*" is used in paste wax polishes, inclusive of those of the silicone-wax type, and in carbon paper. It is used with an equivalent amount of "FT − 200" wax in the formation of water emulsion paste waxes.

Emulsifiable Polyethylene Waxes

An emulsifiable wax (mol. wt. <6000) has been recently commercially produced by the Eastman Chemical Products, Inc., Kingsport, Tennessee, and is known as "Epolene E." This wax has both an acid value and a saponification number of 9–10, which is attributed to "free acid groups . . . built into the polymer molecule." It had been previously found that physical mixtures of ethylene polymers and high molecular weight fatty acids do not make suitable emulsions, and that the chemical structure of the polyethylene wax had to be modified in process of its manufacture.

"Epolene E" has a ring and ball softening point of about 102°C, a penetration hardness (tenths of mm, 100 g/5 sec/77°F) of <1, and a Brookfield viscosity of 1700–1800 cps at 250°F. This wax was specifically designed for water emulsion polishes. The polishes are said to exhibit high gloss, good flowing properties, and resistance to scuff and dirt pickup. Self-polishing formulations contain "Epolene E," saponifying agents, water, and shellac or "Amberol" solution. They contain 3.7 to 8.3 per cent of "Epolene E," and also 0 to 4.5 per cent of "Durez 13560" resin.

"Epolene E" is compatible with natural and petroleum waxes. It is compatible with "Durez 219," and "Durez 13560" resins; it is also compatible with several resins of the nonemulsifiable type, such as "Neville R-29" (coumarone-indene), "Newport V40" (α-pinene), "Piccolyte S-125" (polyterpene), "Arochlor 5460" (chlorinated biphenyl), and "Chlorowax 70" (chlorinated paraffin).

For "Emulsifiable A-C Polyethylenes," see p. 533.

(2) BLENDED WAXES

Ceresin Wax

In the category of mixed or blended waxes, excluding the so-called dairy wax (milk carton wax), the most outstanding commercial item is "ceresin wax." The term *ceresin* or *ceresine* as originally given to the pure white wax refined from ozocerite, lost its significance many years ago. On account of its high price practically no pure ceresin has come into the market. What is called ceresin proved to be paraffin wax mixed with 10 to 30 per cent of pure white ozocerite, and generally a small admixture of carnauba wax to raise the melting point. These mixtures were often colored yellow to re-

semble the pure unbleached genuine ceresin, with oil-soluble colors, such as quinoline yellow, auramine, etc.

In the industrial arts there has always been a demand for more or less plastic waxes of relatively high melting point, viz., 63 to 74°C (145–165°F), which are devoid of any pronounced crystalline (macrocrystalline) characteristics, and which are unsaponifiable or nearly so. To meet this demand the wax converters have offered and continue to offer these so-called ceresin waxes in quantities ranging from the cheapest to the best and more expensive. Ceresin waxes are offered in many colors; i.e., white, yellow, amber, orange, brown, and black.

Normally a wax of 160°F melting point is hard and lacks plasticity as is shown by a needle penetration of about 5. Ozocerite of the same melting point (160°F) is relatively soft and plastic, shown by its needle penetration of about 13.5. The plasticity of the ceresin is controlled by the amount of ozocerite incorporated in the paraffin wax, although partially offset by the addition of a small amount (1 or 2 per cent) of carnauba. For many purposes it is desirable to employ a ceresin which is devoid of a slippery feel, but for the purpose of lubricity it becomes necessary to incorporate in the ceresin wax an appreciable amount of an oily material such as slack wax. The composition of a ceresin wax of this nature has peculiar melting point characteristics. A determination of the drop point, softening point, and ball and ring point, as well as the Fisher-Johns melting point figures often discloses the components of the ceresin. For example, a commercial ceresin (MR 1397) had a melting point of 168.0°F, softening point 105.8°F, and ball and ring point of 140.9°F. The Fisher-Johns melting point was 109.4 minimum, 118.9 spread, and 179.6°F maximum. The low softening point is attributed to the slack wax component, and the maximum Fisher-Johns reading is equivalent to the melting point of carnauba wax, of which it also had a perceptible odor. The color of the wax was ivory-white. A penetration value which was relatively high (30.1 at 100 g/55 sec/25°C) indicates a considerable proportion of slack wax in its composition.

"Polymekon"-Petroleum Wax Blends

"Polymekon" is the trade name of a so-called specially processed petroleum wax containing no polyethylene. It has a yellow color (NPA 3-4), is not saponifiable, and has a melting point of 200°F minimum, and softening point 195–200°F. It is very hard; its penetration value (100 g/5 sec/77°F) is 0 to 3.

"Polymekon" is useful as an additive to paraffin and/or microcrystalline waxes in the coating of papers. The incorporation of 3 per cent of "PM" in a 50:50 mixture of paraffin and microcrystalline waxes is said to give a water vapor transmission of 29 (WVT in/g/sq m/24 hrs) with a seam

strength of 36 g per in. width of wax-coated 30-lb sulfite paper. The incorporation of 5 per cent "PM" reduces the WVT value to 18.9, and the seam strength to 33.5 g per in. width. There is no blocking of the coated papers at 100°F. No difficulty is experienced in the blending of "PM" with other waxes at temperatures slightly above the melting point of the blend, 150–160°F or thereabouts.

Paraffin-Carnauba Wax Blends

Typical of the blended waxes are the paraffin-carnauba wax blends containing carnauba wax as a functional component. Carnauba wax when fused in paraffin wax elevates the melting point of the latter to a pronounced degree, more so than the addition of any other natural wax. The addition of but 10 per cent of carnauba wax will bring the hardness of the resultant mixture to within a few points of carnauba wax itself. The tabulation below is based on a mixture of paraffine (m. 130°F) and carnauba wax (gordurosa).

Per Cent Carnauba	Dry Melting Pt. (°F)	Wet Softening Pt. (°F)	Spread (°F)	Durometer Hardness At 52°F	Durometer Hardness At 73°F
0	130	110	20	77.0	60
1.2	144	113	21	—	—
2.5	170	115	55	—	—
5.0	175	119	56	88.0	67
7.5	177	126	51	—	—
10.0	178	129	48	95.0	74
15.0	—	—	—	96.5	80
20.0	178.5	143	35.5	97.0	85
25.0	—	—	—	97.0	87
30.0	178.5	151	27.5	—	—
40.0	179	153	26	—	—
50.0	179	160	19	97.0	88
60.0	179	166	13	—	—
70.0	179	169	10	—	—
75.0	—	—	—	97.5	89
80.0	179	173	6	—	—
90.0	182	177	5	—	—
100.0	186	182	4	98.0	90

The incorporation of 3 to 5 per cent of carnauba in mixtures of waxes is quite common practice. If 20 per cent of carnauba is added to paraffin wax, the resultant product is quite resistant to water to at least pasteurizing temperature. The addition of higher amounts of carnauba (20–50 per cent) is of no practical value, as the resultant waxes shrink and crack. The incorporation of still higher amount of carnauba produces a very good hard wax suited for industrial use.

Blends of Hydrocarbon and Synthetic Waxes

Dairy Wax. The designation dairy wax, or "milk carton wax," has been given to a preblended wax suited to waxing (a) "flat top" and (b) "slant top" paper milk cartons. The containers are shipped to the dairy either already wax coated and "ready for use," or in printed flat form, whence they are coated and sterilized, inside and out, right in the filling room of the milk plant.

These precut cartons are made by the Ex-Cell-O Corporation, Detroit, Michigan. The machine which the dairy operates is known as "Pure-Pak." The machine opens the carton to its rectangular shape, applies glue to the bottom flaps, and seals them to form a box open at the top. The carton then is waxed by dipping in melted dairy wax (165–185°F), is drained of excess wax, and put through a cooling chamber (35–40°F) to set up the wax. The carton is then filled with milk, and the "gable top" formed and stapled to seal effectively when inverted. About 60 per cent of "Pure-Pak" cartons are of quart size. About 35 pounds of wax are used per thousand quart cartons. In 1953 about 2000 "Pure-Pak" machines were in operation in the United States.

In a factory where the milk cartons are prefabricated they are waxed with paraffine of 126/128°F (ASTM) melting point or other suitable wax. The operation is a continuous one in which the paper is formed into the carton, and then travels down through the wax bath which is held at a temperature of 160°F. After the carton leaves the bath it is drained upside down and chilled at a temperature of 40°F to set the wax. The speed of operation exceeds 350 cartons per minute. Wax is delivered in tank cars or trucks, usually by tank trucks holding 4000 gallons. A plant may be equipped with six holding tanks of 10,000 gallons each capacity, connected individually with the six lines of carton production. The paraffin wax must have a high modulus of rupture (MR), that is, the MR value should exceed 325 psi. Addition of microcrystalline wax or other suitable additive is often needed to bring up the MR value of the paraffine to the required specification.

Where dairies are operating with the "Pure-Pak" single service container machine, the mechanical unit is capable of producing 25,000 or more filled containers in a single shift. The wax used is a fully refined paraffine of 126/128°F or 128/130°F (ASTM) grade to which there has been incorporated an additive; such as microcrystalline wax (2 to 5 per cent), a polyisobutylene polymer (2 per cent), or a low polymer polyethylene (2 per cent), or suitable blends of such additives. Dairy waxes on the market include "Tervan 2850" of the Esso Standard Oil Company, "Dairy Wax" of Quaker State Oil Refining Company, "Sealrite" of Sun Oil Company,

"Durafin" of Atlantic Refining Company, "Amrin" of Sinclair Refining Company, and a few others.

A preblended wax for milk cartons prepared from 98 parts of paraffine (126/128°F) (AMP) and 2 parts of polyisobutylene polymer will have the following physical characteristics: melting point (ASTM) 127–130°F, oil content (ASTM) 0.3 per cent, color (Saybolt) +16, taste—none, odor—none, viscosity (SSU at 210°F) 38, tensile strength 420 psi, modulus of rupture 700 psi, flexibility (0.001-in. units) 66. The modulus of rupture test measures the ability of a wax to resist breakage when a stress is applied to the center of a horizontal bar of the wax supported at both ends.

It has been shown that microcrystalline wax while effective in increasing the tensile strength of some relatively weak paraffin waxes, may actually reduce the tensile strength of other special high-tensile waxes. In one example the addition of 3 per cent of microcrystalline wax to a paraffine of 124°F melting point caused the tensile strength when determined with an "inclined plane" instrument to drop from 370 to 328 psi.

The important properties desired of the wax on cartons are mileage, resistance to cracking, gloss or lack of it, smoothness, resistance to flaking, resistance to bulging, and color. Mileage is influenced by the type of paperboard stock used and the viscosity of the wax. Lower viscosity dairy waxes give lower coating weights. Cartons are used for packaging buttermilk, skim milk, and homogenized milk, as well as for the regular pasteurized milk.

Dairy wax is molded in slabs 12 × 19½ × 1½ inches for use by the dairies. The slabs weigh 10½ pounds. Five slabs are packed in a rectangular shipping carton, or they may be stacked without cartons on pallets so that they may be handled by a fork truck. Larger dairies can use tank cars of molten wax (160°F) if they have suitable storage facilities. In its use in the packaging machines the liquid wax is pumped from a liquid wax storage tank on the premises, the wax being held at a thermostatically controlled temperature. Liquid wax costs the dairy much less than slabbed wax. (F. I. Staff, *Food Ind.*, May 1950). About 400 million pounds of paraffin wax was consumed in 1954 for the packaging of dairy products.

Coating Waxes. Waxes for coating paper and other material are basically paraffines or paraffine-microcrystalline wax blends in which a polyalkene or other synthetic material is incorporated. There are on the market several general utility waxes which are of this nature—designed to enhance all the desirable qualities and eliminate the shortcomings of straight paraffin wax. Generally speaking, they are more glossy, harder, more flexible, and tougher; they are more grease resistant, waterproof, and moisture-vapor resistant, especially on packages which have folds or creases, and most commercial packages are in this category. An example is "Parafflex

Wax" of the Boler Petroleum Company of Philadelphia, Pa. These waxes are manufactured at the refinery and shipped as ready-to-use material. They are offered as tasteless, odorless, and nontoxic waxes.

Waxes of this kind are used in the paper industry in two basic ways. The first is called "dry-waxing" and refers to the impregnation of paper with wax below the surface or in the body of the sheet. Such a sheet is waterproof but not moisture-vapor-proof. An example of the use of this sheet is in the wrapping of fresh meat, the sheet being known as "butcher's wrap." The furnish of the butcher's papers is usually 50 per cent or more of unbleached sulfite pulp, the rest ground wood.

The second and more important way that a wax of the "Parafflex" type is used is in "wet waxing" where a continuous film is applied to the sheet to render it both waterproof and moisture-vapor-proof. Familiar examples of this are paper milk cartons, frozen food packages, bread wrappers, and the like. In these cases the protective qualities of the wax are utilized in the preservation of the food from deterioration or moisture loss and consequent staling.

In waxing paper, "Parafflex Wax" has an operating temperature of 200–210°F, or a little higher temperature than straight paraffin wax. It is completely protected from temperature breakdown and oxidation by nontoxic stabilizers. Chilling after application of the wax is essential to develop optimum gloss, as for example in producing household rolls of waxed paper. Waxed paper sold in the food stores in 1950 amounted to $36,324,000.

"Parafflex" and similar waxes are used extensively in the United States for bread wrappers, cartons for butter, oleomargarine, lard, ice cream, and other foods, where grease resistance and protection from moisture loss at refrigerator and room temperatures is required. Other uses are paper drinking cups, vegetable trays, and cake and bakery boards.

"Estawax." "Estawax" is a trade name for a wax sold by the Petrolite Corporation, New York. The supplier suggests its use in phonographic records, solvent paste, and liquid polishes.

Cork Tile Wax. Cork tile wax is a blend of microcrystalline and polyethylene waxes. It is used by the manufacturer in finishing linoleum and other flooring material. It has gloss, non-slip, and scuff-resistant properties.

Polybutene in Waxes. The term *polybutene* $(C_4H_8)_x$ as here implied includes one or more polymers, or mixtures of same, of *1*-butene $(CH_3 \cdot CH_2 \cdot CH{:}CH_2)$; *2*-butene $(CH_3CH{:}CHCH_3)$; or *iso*butylene (*methylpropene*) $(CH_3)_2C{:}CH_2$. Polybutene of very high molecular weight (Staudinger 50,000 plus) can be blended with hydrocarbon waxes, preferably fully refined paraffin wax, to produce greatly improved characteristics.

Polybutene is commercially produced by the treatment of isobutylene containing olefinic mixtures, condensed at temperatures ranging from

−40 to −100°C, with a Friedel-Crafts type of catalyst, such as boron fluoride or aluminum chloride. The resultant polymer is a plastic, elastic solid of high molecular weight. The softer solid polymers have a molecular weight ranging from 1000 to 10,000, whereas the harder polymers have a molecular weight in the range of 10,000 to 250,000. The material in general shows a substantial tackiness, has the property of cold flow, and possesses little or no thermal plasticity. Likewise, by virtue of the cold flow it has a low physical strength.

"Vistanex K" is the designation for a series of light-colored polymers which vary in consistency from light oil to a very viscous liquid, products of the Enjay Company, Inc., New York. They grade from K-3 with a mean molecular weight of 330 to K-9 with a molecular weight of 940. The Saybolt viscosity at 210°F ranges from 40.6 to 1010 seconds, according to grade. These polymers have excellent dielectric properties.

Ten per cent of "Vistanex K-5" is compatible with spermaceti, carnauba wax, montan wax, palm wax, ceresin, and ozokerite, as well as with many resins. "Vistanex" of a soft, sticky, but substantially solid consistency usually has a molecular weight of 10,000 to 100,000. A polybutene of 60,000–65,000 molecular weight is often used as an additive to paraffin or other waxes for industrial applications. Since the blending of polybutene with wax is somewhat difficult, the wax refiner has placed on the market certain polybutene-paraffine concentrates preblended for use by the consumer with other waxes. For example, 25 per cent of a polybutene of 60,000 molecular weight may be blended with 75 per cent of paraffin wax. This preblended wax may be dissolved in the finishing wax by the consumer with a minimum of time and effort. In many finishing wax formulations not more than 10 per cent of the above concentrate would be used so that the finishing wax would contain only 2.5 per cent of the polybutene. If higher amounts of such concentrates are employed the mixtures become too viscous for coating purposes.

Prewar use established three main grades, which for convenience will be referred to as A, B, and C. Grade A wax is of low molecular weight and is viscous, soft, and sticky. It has the unique ability to laminate waxed paper to paperboard and the like. Thus in jar-top liners it will hold a heavily waxed sheet to chipboard. A prewar use was in preventing the scuffing and flaking of paraffin wax on bread wrap. The gloss and hardness of bread wrap wax is greatly improved by combining polyethylene with polyisobutene (see Polybutene-Polyethylene-Wax Blends, p. 508). Grades B and C comprised tough elastic grades of polybutene in fully refined paraffin wax of different melting points. B had a melting point of 55–56°C (132°F), whereas C had a melting point of 60°C (140°F), the latter being used with cellophane films.

Polybutene has been advantageously blended with microcrystalline wax. As a modifier for solid paraffine, polybutene improves bread wraps, frozen food packaging, and paper milk containers, and increases end seal strength and tear strength of bread wrappers. Polybutene wax blends have also been used for prelabel cheese wraps. In its pure form, polybutene is so cohesive and adhesive that handling is not simple, therefore blending of paraffin wax is done by the converter by using commercially concentrated grades previously mentioned that are capable of extensive dilution with additional paraffine in the equipment regularly used for paraffin wax.

Polybutene-wax blends may also be dissolved in a hydrocarbon liquid solvent and applied as a coating to sheet material. Thomas[19] describes a coating composition for use on paper, regenerated cellulose film (cellophane), leather, etc., from a polymer of butene (preferably of about 65,000 molecular weight), *scale wax*, and a solvent such as gasoline, benzin, or VM&P naphtha. Waxes other than scale wax may be used, e.g., *paraffine* 140°F-AMP, *carnabua*, *ceresin*, *montan*, *ozocerite*, etc. He states that similar formulations can be made by employing the butadiene polymer known as "buna," with wax. When using isobutylene polymer ("Vistanex") it should be suspended in a solvent and added to the liquified paraffin wax. (Also see Polyethylene and Polyisobutylene Plastic Wax Films.)

Lower-Polymer Polyethylene-Paraffin Wax Mixtures. The later art has taught that the use of the lower solid polymers of ethylene (i.e., mol. wt. below 4000) as additives to waxes not only simplifies blending but secures a better dispersion of the polyethylene in the finished wax that is to be applied to paper or other material. The use of lower-polymer polyethylene elevates the melting point of paraffin wax and increases its hardness as shown in Tables 71–76.

"Morax." "Morax" is a trade name (of Moore & Munger, New York) given to a polyethylene concentrate to blend in with paraffin waxes of the type generally used for milk cartons. "Morax" is a predispersed concentrate of polyethylene (resin) in paraffin wax, whereas "Morax N" is a concentrate consisting essentially of polyethylene (resin) and microcrystalline

TABLE 71

% "A-C Polyethylene #6"	% Paraffine 128/130	Solidification Point (°F)		Needle Penetration 200 g/5 sec/25°C
		Empirical	Theoretical	
0	100	125–127	125–127	32.3
5	95	130–132	129–130	30.3
10	90	136–138	134–136	28.8
20	80	149–151	144–146	24.3
30	70	163–165	153–155	19.8
40	60	176–177	163–165	15.3
100	0	219–221	219–221	2.3

TABLE 72

% "A-C Polyethylene #6"	% Paraffine 134/136	Solidification Point (°F) Empirical	Solidification Point (°F) Theoretical	Needle Penetration 100 g/5 sec/25°C
0	100	133–135	133–135	15.6
1	99	134–136	134–136	13.9
2½	97½	136–138	135–137	12.7
5	95	134–141	138–140	11.6
10	90	145–147	142–144	9.5
20	80	157–159	152–154	7.8
40	60	184–186	170–172	5.2
60	40	—	189–191	3.8
80	20	—	208–210	2.6
100	0	219–221	229–221	1.6

TABLE 73. ADDITION OF POLYETHYLENE WAX (EXTRA HARD, ABOUT 2000 MOL. WT.) TO PARAFFIN WAX (133–135°F AMP)

Per Cent Polyethylene	Melting Point °C	Melting Point °F	Durometer Hardness (25°C)	Needle Penetration (mm × 10) 100 g/5 sec/25°C
0	57.5	135.5	72	15.0
1	59	138.2	77	12.0
2	59.5	139.1	78	11.0
5	61	141.8	81	9.0
10	66	150.8	86	6.0
20	75.6	168	92	3.8
40	88	190.4	97	2.3
60	94.5	202	98	1.9
80	98.3	209	99	1.5
100	105	221	100	0.9

TABLE 74. EFFECT OF THE INCORPORATION OF 2 PER CENT OF "A-C POLYETHYLENE #6" TO PARAFFIN WAXES OF VARIOUS MELTING POINTS

Designation of Sample	Melting Point (°F) None Added	Melting Point (°F) 2% Added	Hardness (D) None Added	Hardness (D) 2% Added	Penetration (100g) None Added	Penetration (100g) 2% Added
A121	107–6	107.6	0	0	70	66
A141	120.2	124.7	38	40	32	30
CS 125/127	127.4	130.0	55	64	16	14
T 130/137	131.0	138.2	65	70	14	12
A191	134.6	138.2	68	75	11	9
T 133/135	135.5	136.4	67	73	10	8.5
SU 133/135	135.5	139.1	72	77	12	7
SO 150	153.0	157.0	—	—	—	—

Note: Translucent appearance of paraffin waxes changes to an opaque white with an addition of 2 per cent of polyethylene wax. Only 1 per cent of polyethylene wax was required to remove brittleness from the higher melting paraffines.

TABLE 75. EFFECT OF THE INCORPORATION OF INCREASING AMOUNTS OF POLYETHYLENE WAX IN A PARAFFIN WAX (125/127°F AMP)

% "A-C Polyethylene #6"	Melting Point (°F)	Penetration (100 g/5 sec/77°F)	Hardness by Durometer
none	127.4	19.5	45
1	129	16.6	57
2	130	14.4	64
3	130.7	13.1	70
5	131	12.0	75

TABLE 76. "DYDT WAX" ADDED TO MICROCRYSTALLINE WAX, AMBER 170/175

Per Cent "DYDT Polyethylene" (mol. wt. 4000)	Viscosity (SSU) at 275°F
0	52.4
1	53.4
2	54.7
4	58.5
6	64.3
8	71.9
10	81.8

Note: "A-C Polyethylene" is a product of the Semet-Solvay Petrochemical Division of the Allied Chemical and Dye Corporation; "DYDT Polyethylene" is a product of the Bakelite Corporation.

wax. Both may be blended with dairy grades of paraffin wax, to the extent of ½ to 3 per cent. "Morax" is preferred to "Morax N" when the dairy wax already has some microcrystalline wax as an ingredient. Polyethylene concentrates when added to paraffin wax are said to improve tensile strength, increase viscosity slightly but improve flow properties, increase congealing point slightly, and improve texture. They do require mild agitation to keep them from settling to the bottom of the tank, if the blended wax is held at a temperature below the cloud point.

The softening points of "Morax" and "Morax N" are 206° and 213°F respectively. The viscosities at 250°F are 7000 and 9000 cp respectively.

Polybutene-Polyethylene-Wax Blends. Sparks[17] has pointed out the advantages that may be gained in improving the physical characteristics of polyisobutylene by incorporating a substantial amount of polyethylene. Polyethylene $(CH_2)_x$ is produced by condensation of the ethylene at elevated temperatures and extremely high pressures ranging from 1000 atmospheres upward. The material is thermoplastic at temperatures above 130°C and is quite tough. It is, however, relatively inelastic, and readily broken. The molecular weights are usually of the order of 15,000 to 20,000. When a solid solution of polyethylene and polyisobutylene (40 to 60 parts) is

TABLE 77. PROPERTIES OF BLENDS OF "MORAX" WITH PARAFFINE OF 128/130°F MELTING POINT*

	Per Cent	"Morax"	"Morax N"
Cloud point	1	158°F	163°F
	3	162	167
	5	166	172
Congealing point	0	128°F	128°F
	1	128	131
	3	135	134
	5	143	145
Tensile strength	0	284 psi	284 psi
	1	430	426
	3	488	458
	5	554	498
Viscosity @ 175°F	0	6.0 cp	6.0 cp
	1	6.5	7.0
	3	8.0	9.0
	5	10.0	13.0

* Taken from "Technical Bulletin" (1955) of Moore & Munger.

produced the composition is highly insoluble, moderately elastic, tough, nonbrittle, and thermoplastic.

A suitable quantity of polyisobutylene ("Vistanex Polybutene") having a molecular weight of 200,000 is brought to a temperature of 110–120°C by milling the polymer under the ordinary double roll rubber mill. The milling is continued until the polyethylene is thoroughly dispersed through the polyisobutylene and until a clear, homogenous mixture is obtained. The mill is desirably cooled to a temperature of 50–70°C and the total time of milling can be kept within 20–25 minutes. The material can be sheeted for wrapping purposes; the package with its contents may be thermosealed and sterilized at temperatures up to 105°C. The composition will soften at 130–150°C.

To the polyisobutylene on the mill may be added 1 to 25 parts of paraffin wax, and thereafter 30 to 60 parts of polyethylene, and the milling continued until a homogenous mixture is obtained. The resultant material is transparent, tough, flexible, somewhat elastic, and highly insoluble. The melting point is substantially reduced, and with an ample amount of paraffin wax the melting point of the composition may be brought as low as 75°C (167°F).

The Sparks composition[17] of polyethylene with polybutene is generally referred to in the trade as "S-polymer." *S-polymer* raises the melting point of waxes, tends to stabilize them from breakdown with heat, improve their

flexibility, and in some cases lower their permeability to water vapor. High polymer concentrations in waxes have shown considerable promise for cellophane coatings, wax paper laminates, and adhesives for paper labels that are applied to cardboard and on cellophane containers by heat and pressure. Low polymer concentrations in waxes have been successfully used for bread wrappers.

"*Tervan 2800*" is paraffine in which about 25 per cent of B60 polybutene (60,000 m. wt.) has been incorporated. Schneider and his associates[14] of the Esso Standard Oil Company developed a means of obtaining a homogenous three-component mixture of wax, polyisobutylene, and polyethylene for use as a waterproof coating for paper or fabric. The polymers are milled, the mixture is placed in a hot kneader, and the molten wax is added, dropwise at first and then at increasing rate. The solid mixture melts at 120–150°C, is readily absorbed by paper or fabric, and gives a strong heat seal in the wrapper. Stacked sheets treated with the three-component mixture show little tendency to blocking.

"Arwaxes." "Arwax" is a trade name given to preblended waxes of the American Resinous Chemicals Corporation, Peabody, Massachusetts. The elastomer in the preblended wax may be polybutene, polyethylene, S-polymer, or the like. "*Arwaxes*" are light in color, tasteless, odorless, elastic, heat stable, chemically inert, and compatible with *paraffin, microwax, petroleum ozokerite, etc.*

"Arwax (717-46B)" is a homogenous concentrate of butyl rubber dispersed in 138–140°F (AMP) paraffin wax. Fifteen parts by weight of "Arwax" blended with eighty-five parts of 138–140°F paraffine has a viscosity of about 30 centistokes at 210°F; 25 parts of "Arwax" blended with 75 parts of 138–140°F paraffine has a viscosity of about 110 centistokes at 210°F. "Arwax" added to paraffine acts as an antiblocking agent, improves vapor resistance of folded waxed papers; and the use of 20 parts of "arwax (717-46B)" with 80 parts of 138–140°F paraffine develops a strong bond at 200–250°F in heat-sealing coated glassines; as for the "slug pack" (individually wrapped ¼ pounds) by cracker manufacturers.

Sulfite paper (25 pounds per ream) coated with a blend of paraffin wax (133–135°F, AMP) and 7.6 per cent "Arwax," equivalent to 2 per cent in the finished coating, has shown a WVP (water vapor penetration) value of 0.15 and 1.5 for the creased paper. Plain paper controls showed WVP values of 0.52 for uncreased and 3.15 for creased papers. WVP values are expressed as grams of water per 100 square inches per 24 hours penetrating through specimen under test. The application wax with a 5 per cent "*Arwax*" content to one side of parchments and glassines is said to have given quite satisfactory results for frozen food wrappings. Such wax-coated papers are also easily heat sealed.

(3) COMPOUNDS OF WAX WITH NONWAX MATERIALS

Resin-Wax Mixtures

Various mixtures of natural resins with waxes and waxlike substances were studied by Allan[2]. The resins were commercial grades of damar, Manils, fused Congo, kauri, and elemi. The waxes comprised *beeswax*, *carnauba wax*, *montan wax*, *japanwax*, *ozocerite*, and *paraffin*. In general, the resins are completely miscible in the waxes studied, although certain of the fossil resins, and some Manila resins, are not at all compatible with paraffin. Synthetic resins are often mixed with natural and/or hydrocarbon waxes to produce mixtures useful in the arts and industries.

Resins which are completely miscible with microcrystalline petroleum waxes are "Flexalyn," "Pentalyn," "Poly-pale Ester Gums," "Staybelite Ester Gums," "Abalyn," and "Hercolyn" (all of Hercules Powder Company); "Dow Resins" (Dow Chemical Comapny); "Ester Gum," "Fused Congo," and "Congo Ester" (U. S. Industrial Chemicals Company); "Pliolite Resin S" (Goodyear Tire & Rubber Company); "Nypene" and "Neville Resin" (The Neville Company); "Durez Resin" (Durez Plastics & Chemicals, Inc.); "Aroclor" (Monsanto Chemical Company); "Vistanex" (Enjay Company); "Vistac" (Advance Solvents & Chemical Corporation).

An example of a good blend of resin-wax is that prepared from "Durez Resin 219" 10 parts, and *carnauba wax* 90 parts; it is said to give a harder, glossier water emulsion polish. Coumarone-indene resins ("Cumar") are blended with waxes. Adulteration is practised by adding such relatively inexpensive material to more expensive waxes such as carnauba.

Resin-wax mixtures find application in coating, sizing, and impregnating paper; in transfer inks, in polishes, and candles; in molding and waterproofing compositions; and as linings for metal food and beverage containers. The mixtures can be emulsified with triethanolamine, or other alkaline compounds that will form soaps.

Polymerized rosin is esterified and combined with wax to produce hot melt coatings. Polymerized rosin is rosin which has been polymerized in solution by agents such as sulfuric acid; boron trifluoride; anhydrous aluminum, tin, zinc, or titanium chlorides; or by ultraviolet light. The esterified polymerized rosin is prepared from polymerized rosin and glycerine, or any of the glycols, e.g., by heating together 90.5 parts of molten polymerized rosin and 9.5 parts of glycerine, and maintaining the temperature at 280°C for a suitable time. The wax compounded with the rosin derivative is ordinarily paraffin, but carnauba, candelilla, beeswax, montan, ozocerite, stearic acid, and cetyl or stearyl alcohol may be used in its place. Ester gum made from plain rosin may be mixed with wax, but does not

form permanently stabilized compounds; that is, there is a tendency for the constituents to separate on remelting.

Esterified polymerized rosin-wax compounds can be used for coating paper, cloth fabric, and other surfaces, by hot application of the compound employing a grooved or other suitable metal roll. Papers so coated may be used for food wrapping as they are nontoxic.

A rosin-microcrystalline wax composition for filling up the meshes of reticular sheets can be readily made, according to Warp[20], by melting together 2 parts of natural water white rosin (m. 170°F), and 1 part of *microcrystalline wax* (m. 160°F).

Illustrative of a resin-wax mixture in which a synthetic resin is employed is a composition proposed for coating paper by the Canada Paper Company and Szwarc[5]. In their patent specifications it is claimed that the composition is flexible, water-vapor resistant, and printable, and will retain its flexibility at −20°F. It consists of *coumarone-indene resin* 55–65, ethylcellulose 8–12, rosin ester plasticizer 8–12, *paraffin wax* 8–12, and zinc stearate 1–3 parts.

Many synthetic resins can be made compatible with hydrocarbon waxes such as paraffin and micro waxes, by using fatty acid amides (e.g. "Armids") as mutual solvents.

Acrylic resins may be combined with *ceresin wax* and other waxes to produce thermoplastic coatings on metal and cellulosic material. The Imperial Chemical Industries, Ltd.[10], has patented a thermoplastic coating material which may be made by heating and thoroughly mixing a hydroxystearic acid ester (e.g., 12-hydroxystearin produced by the catalytic hydrogenation of castor oil) with a polymeric acrylic or methacrylic ester of an aliphatic alcohol (i.e., polymeric butyl or isobutyl methacrylate). These compositions can also be effectively blended with other wax-resin compositions.

The addition of a *wax* to a *polystyrene* composition above normally compatible amounts makes it possible to produce sound records superior to those made of shellac. This is done by heating the compositions above the temperature encountered in the molding process. [Groff, F., Potter, P. B., Smith, R. W. (to Union Carbide & Carbon Corp.), U. S. Patent 2,681,323 (1954).]

"Pliowax"

"Pliowax" is a combination of "*Pliolite Resin*" and paraffine, and is prepared by incorporating the unmilled resin powder into paraffin wax. Thies[18] has given x-ray diagrams of "Pliolite" and mixtures of "Pliolite" and paraffin wax at different temperatures. The solubility of wax in "Pliolite" increases with increase in temperature to the melting point of the wax, whereupon they become miscible in all proportions. These mixtures, namely "Pliowax," are tougher and in films are more lustrous than the wax alone.

"Pliolite" resin is a synthetic derivative of rubber which is formed by a cyclization process. "Pliolite" results from a reaction between crepe rubber and a tin salt, such as stannic chloride or chlorostannic acid. It has the same ultimate chemical composition as the natural rubber from which it is derived, but it does differ in its structural formula: the aggregation of the isoprene (C_5H_8) molecules is cyclic in the case of "Pliolite."

The process of preparation of "Pliolite" (Marbon Corporation, Delaware)[7] involves dissolving the rubber with a suitable solvent to form a heavy, viscous, nondrying cement. The rubber cement is then placed in a jacketed reactor equipped with a reflux condenser and heated for a period of time with a reactant and catalyst; e.g., hydrochloric acid and anhydrous stannic chloride. During the heating period an enormous reduction in the viscosity of the solution is experienced and a physical change is effected from the usual rubber into the resinous state. The reaction is stopped by water and the resin is recovered from the solvent as a finely divided powder which is vacuum dried. The powder is milled to yield solutions which will produce heat-sealing film materials, but if admixtures of "Pliolite" and wax are desired, where wax is to predominate, it has been found that the "Pliolite" resin powder very readily dissolves in most of the common waxes, by simply heating the wax and then adding the unmilled resin. "*Pliolite*" is not to be confused with "*Pliofilm*," which is a plasticized rubber hydrochloride, a product of the Goodyear Tire & Rubber Company.

"Pliowax" is gray-brownish in color, but is nearly white in thin film form. It contains 20 to 30 per cent of "Pliolite" resin. The melting point is somewhat higher than that of the paraffin wax from which it is prepared. The addition of unmilled "Pliolite" resin to a paraffin of 134/136°F AMP grade is said to increase its melting point 3 degrees for every 5 per cent of "Pliolite" added. However, it is not certain whether such an increase in the melting point would persist in the seasoning of the "Pliowax." "Pliowax" containing 25 per cent of milled "Pliolite" (Goodyear Tire & Rubber Company) had a melting point of 56°C (132.8°F) and a softening point of 45°C (113.0°F), a durometer hardness of 95 at 24°C (76°F), and a specific gravity (d_{15}^{5}) of 0.9372. The wax showed good plasticity and elongation at a temperature of 45–49°C. Another sample which assayed 29.1 per cent of rubber resins had a hardness of 70 at 24°C, and 90 at 0°C; it melted at 57°C (134.6°F).

"Pliolite" resin may be incorporated in *petrolatum*, *beeswax*, *ceresin*, or hydrogenated oils in part or as a whole to replace paraffin wax, although "Pliowax" per se is essentially a blend of "Pliolite" with paraffine. The viscosity of "Pliowax" melts is higher than of paraffine, and the molten wax adheres to smooth surfaces more tenaciously than does paraffine. There is also less tendency of "Pliowax" to penetrate the material that is coated, and the waxed surface is tougher and is less apt to crystallize.

"Pliowax" may be diluted with further quantities of wax simply by melting the materials together. This is best accomplished at a temperature not over 180 or 190°C to prevent any deterioration. From the x-ray diffraction patterns Thies[18] found that "Pliolite," when present in 9 to 10 per cent, gives a true solution with paraffin wax at room temperature. A film of

"Pliolite" and paraffine (90:10) is optically clear even though the x-ray pattern does not show the crystalline paraffin ring to be present.

"Pliowax" is applied to sheet wrapping materials and the like by a hot dip process similar to the conventional process of paraffining. Even with low concentrations of "Pliolite" in the "Pliowax," the adherence of the coating is appreciably increased and the waterproofness of the waxed paper is greatly enhanced. According to the Goodyear Tire & Rubber Company, the "Pliowax" product is useful in the processing of paper milk cartons and fruit juice containers, frozen food packages, and the coating of paper for bread wrap. "Pliowax" may be used as a cheese coating. Greaseproof coatings may be applied to paper or cardboard not only for waterproofing, but for heat sealing, and these containers may be used for fats and oils.

"Pliolite"-Wax. "Pliolite"-wax is the designation given to a composition which differs somewhat from "*Pliowax*" in the following manner: Instead of fusing *unmilled* "Pliolite" with wax by heating them together, the wax is incorporated in *milled* "Pliolite" on mixing rolls, or in a Banbury mixer. A particular advantage of this process is that it broadens the scope of application, since small amounts of other material may be incorporated in the "Pliolite"-wax during the milling, when and as desired.

In milling, the "Pliolite" powder, a finely divided white material, is massed by passing through a tight mill once, and then is banded slowly on the mill until the thermoplastic mass forms a bank. To make rubber-"Pliolite" mixtures, it is necessary to put the "Pliolite" on first, and add the rubber slowly in the beginning until approximately 10 to 15 per cent of the rubber is in the batch; then the relative speed of rubber addition can be reached. The wax is incorporated in the desired quantity and the batch completed.

"Pliolite"-wax is suited to laminating paper boards, since it will form a water-insoluble bond between the plies and give flexibility to the resultant plyboard. Added to paraffine, "Pliolite"-wax prevents crystallization. Its use has been suggested for the making of mounts, wherein its tough viscous properties make it less liable to flow in warm weather than paraffin wax.

Paper sheet material coated with "Pliolite"-wax is nonblocking, and can be made heat-sealing when ironed or otherwise heat-treated. These characteristics are of value in the design of waterproof paper packages to be used in the packaging of cereals, dehydrated foods, etc.

"Pliolite"-wax, or "Pliolite" plus paraffin wax, dissolved in a suitable solvent, can be applied to the surface of freshly prepared concrete, making it substantially impermeable to water and retarding the evaporation of water from the concrete, thus enabling it to cure properly. This is the method of Scripture[15]. Scripture gives several compositions, e.g. xylene 1

gallon, rubber resin ("Pliolite") ⅔ pounds, and paraffin wax 1 ounce. On drying this leaves a film containing 91.5 per cent rubber resin, and 8.5 per cent wax. A suitable coating for a concrete floor may be prepared from xylene 1 gallon, rubber resin ("Pliolite") 1 pound, "Halowax" 1½ pounds, pigment 10 ounces. The application may be made by brushing or spraying.

Wax-Rubber Mixtures

Because of the difficulty encountered in mixing rubber with wax without the use of milling or other suitable equipment, the custom is to employ rubber-wax concentrates which can be advantageously blended with other waxes by simple agitation by the paper converter. Typical of rubber-wax concentrates are the "Sealz Waxes" of Dispersion Process, Inc., in which the rubber has been incorporated in hydrocarbon waxes of high melting point, such as paraffin of 140/142°F AMP grade, or on the other hand petrolatum wax 160/165°F ASTM grade. The proportion of rubber to wax is 25:75. A "Sealz Wax" made with refined paraffine showed a melting point of 176°F, one with a petrolatum wax a melting point of 188°F. The rubber used is believed to be unvulcanized. The durometer hardness of a "Sealz Wax" of the lower melting description was found to be 92 at 36°F and 75 at 76°F; that of the higher melting point was softer. The hardness of the latter was 70 at 36°F, and 45 at 76°F, probably because of the softness of the petrolatum wax used in its composition.

"Sealz Waxes" in small amounts can be advantageously blended with other waxes to increase the melting point of the latter. In the concentrate, the presence of each 5 per cent of rubber in the wax increases the melting point by 5 degrees Fahrenheit.

A coating composition of wax-rubber is prepared by melting paraffin wax and adding 6 to 30 per cent by weight of rubber, while the temperature of the melt is held at 180 to 200°F. A Werner-Pfleiderer mixer is used to incorporate the thin, pale, crepe rubber sheets. The composition is being used as a coating for flexible waterproof film materials useful in food packaging. Application of a wax-rubber coating to a rubber hydrochloride film makes it odorless and tasteless in relation to the food it contacts. According to Abrams *et al.*[1], the wax-rubber composition while hot is applied to the "Pliofilm"; a translucent sheet results which may be stretched 400 per cent of its original length without damaging the base sheet or coating. A further advantage of the wax-rubber coating is that its fusion point is below that of the base, and it is thus possible to heat-seal "Pliofilm" in packaging without distorting the chlorinated rubber film.

An attempt has been made by Snyder[16] to incorporate an excess of paraffin or other wax in a rubber hydrochloride cement, and then to cast a film on paper from the cement, simultaneously evaporating the solvent to

produce a film which has a coating of the wax on the surface from which the solvent has evaporated. The cement may be prepared by dissolving rubber hydrochloride in a solvent of the benzene type, with the aid of heat of about 55–65°C for the number of hours sufficient to homogenize it, to make it suitable for coating on paper to be used for wrapping various foods or other products.

Wax Concentrates Containing Polyethylene

Since difficulty is sometimes encountered in incorporating and dispersing one or two per cent of polyethylene in paraffin wax in the wax tank of paper coating equipment, or for other purposes, it becomes convenient to add the polyethylene in a form of a concentrate that will have a melting point of 140–150°F and hence melt readily when added to the hot paraffin bath. A suitable concentrate of polyethylene and paraffin wax additive will contain 20 to 25 per cent polyethylene; a suitable concentrate of polyethylene and microcrystalline wax additive will contain 10 to 15 per cent of polyethylene. Usually only about 10 per cent of the additive is added to the working bath for paper or foil coatings.

Superpolymer Polyethylene-Paraffin Wax Mixtures

According to the early experiments of Lovell in blending superpolymer polyethylene of a high fusion point with paraffin wax, the paraffine should be heated slowly to a temperature of 320°F and the polyethylene added a little at a time. When polyethylene of 470°F (243°C) melting point is added to paraffin wax of 138–140°F melting point, wax mixtures are obtained with melting points shown in Table 78. When 33⅓ per cent of the

TABLE 78. MELTING POINTS OF SUPERPOLYMER POLYETHYLENE-PARAFFIN WAX MIXTURES

Per Cent Polyethylene	M.P. (°F) Empirical	M.P. (°F) Theoretical
2	141.0	145.0
5	148.0	154.8
10	158.5	171.0
14	171.0	183.8
19	191.5	200.0
20	201.5	202.0
30	209.5	236.0
40	216.5	268.5
60	239.5	334.5
70	263.0	366.0
80	308.0	399.0
90	389.0	432.0
95	428.0	448.0
99	459.0	462.0

superpolymer polyethylene content is reached the melting point is 212°F, or lower than the computed melting point (245°F). With a polyethylene content of 20 per cent the empirical and theoretical values are about the same. Even at the higher temperatures a considerable proportion of the high fusion point polyethylene does not blend well with paraffin wax, as is shown in Table 78.

Viscosity of Polyethylene-Petroleum Wax Mixtures

The viscosity, and to a lesser extent the cloud point, is often a determining factor as to whether a blend of polyethylene and petroleum wax can be applied successfully for the coating of paper or other material. For example, if the viscosity (SSU) were limited to 65 seconds at 210°F then not more than 4 per cent of a polyethylene of 12,000 molecular weight would be incorporated in a paraffin wax of 133–135°F melting point, nor more than 4 per cent of a polyethylene of 7000 molecular weight in a microcrystalline wax of 170–175°F melting point. For certain types of application of wax to paper the allowable viscosity is less than 55 seconds, making it imperative to use polyethylenes of 4000 or lower molecular weight in wax mixtures of 140°F or higher melting point. The viscosity of a wax mixture may, however, be lowered by increasing the temperature of the wax bath as is shown in Table 79, provided the polyethylene is kept in a state of dispersion.

TABLE 79. VISCOSITY (SSU) OF 133/135 PARAFFINE WITH ADDED POLYETHYLENE OF 12,000 MOLECULAR WEIGHT

Per Cent "DYLT Polyethylene" (mol. wt. 12,000)	Viscosity (SSU) at 210°F	Viscosity (SSU) at 275°F
0	39.0 sec	33.8 sec
1	42.0	36.8
2	47.3	40.2
4	63.9	46.9
6	85.3	55.9
8	129.4	70.8
10	194.5	98.0

The viscosity of blends of polyethylene with petroleum wax is influenced greatly by the molecular weight of the ethylene polymer as is shown in Tables 80, 81, and 82.

TABLE 80. MIXTURE OF PARAFFINE 133/135 WITH VARIOUS POLYETHYLENES VISCOSITY (SSU) AT 210°F IN SECONDS

% Polyethylene Incorporated	Molecular Weight			
	2000	4000	7000	12,000
0	39.0	39.0	39.0	39.0
4	40.5	42.5	46.5	63.9
10	57.0	68.0	86.0	194.5

TABLE 81. VISCOSITY (SSU) AT 210°F FOR MIXTURES OF MICROCRYSTALLINE WAX, AMBER 170/175, WITH VARIOUS POLYETHYLENES

% Polyethylene Incorporated	Molecular Weight			
	2000	4000	7000	12,000
0	52.4	52.4	52.4	52.4
4	56.5	58.5	62.0	86.5
10	73.5	81.8	122.0	283.7

TABLE 82. SAYBOLT AND KINEMATIC VISCOSITIES OF LOW MOLECULAR WEIGHT POLYETHYLENE MIXED WITH MICROCRYSTALLINE WAX 170/175

% "A-C Polyethylene #6, Hard" (mol. wt. 2100)	Viscosity at 275°F	
	SSU in sec	Kinematic in cks
0	52.4	8.1
1	53.0	8.4
2	53.8	8.6
4	56.5	9.4
6	60.2	10.4
8	65.6	11.6
10	73.5	13.6

Alkylated Polystyrene-Hydrocarbon Wax Mixtures

Butler[4] discovered that polystyrene, polymer of $C_6H_5CH:CH_2$, which has been alkylated by reaction with polymeric propylene, $CH_2:CH\cdot CH_3$, in percentages of preferably less than 40, is completely compatible with hydrocarbon waxes. Preferred mixtures have 80 or more per cent of the hydrocarbon wax, such as paraffin, ceresin, or ozocerite. The polystyene preferred by Butler is one with a molecular weight of 60,000–300,000; it is alkylated with a polymerized propylene (preferably the trimer of b.p. 175–225°C), and the product mixed thoroughly with the hydrocarbon or other wax.

A paper with a high gloss surface, useful as a decorative wrapping material in food packaging, was made by coating paper with a blend of the following materials: alkylated styrene 15, paraffin wax (146/148°F AMP) 34, terpene resin 16, dioctyl phthallate 5, and pigment 8 parts. A coated paper useful in wrapping bread and other foodstuffs by reason of its adhesive nature was prepared by blending: microcrystalline wax (170/175°F ASTM) 20, alkylated polystyrene 8, and paraffin wax (146/148°F AMP) 72 parts. The compositions described may be applied to paper, textiles, or other fibrous material by dipping it into the molten composition, or in solutions of the composition in suitable solvents. It is claimed that alkylated styrene improves the gloss, adhesiveness, hardness, tensile strength, and elongation characteristics of wax coating compositions.

Silicone—Wax Compositions

Under ordinary conditions it is impossible to incorporate more than 0.01 to 0.5 per cent of a silicone oil in petroleum waxes, without having the

silicone bleed out sooner or later. Some improvement takes place with the addition of a suitable resin, of an alkyd resin type. Silicone, because of its marked lubricity, enables the manufacturer to produce a self-polishing wax, or one which requires but a single rubbing application to the table top or other surface. Such polishes are prepared from silicone oil in proportion of upward of 0.5 per cent, hydrocarbon solvent, water, and a suitable emulsifying agent.

The term "silicone" is given to a large variety of polymers built on a structure of alternate silicon and oxygen atoms with various organic groups attached to the unsaturated valences of the silicon atoms. All of the silicones may be represented by the empirical formula:

$$R_xSiO\left(4-\frac{x}{2}\right)_n$$

where x is the number of molecules of R. The R of the structural unit R_xSiO is usually CH_3, or C_2H_5, but may be H, C_3H_8, C_6H_5 or more complex substituents. Commercial silicones are mostly methyl silicones such as $MeSi(OSiMe_2)_nSiMe_3$ ("Dow Corning type 200 Fluid"). The polyorganosiloxanes are produced in a wide variety of physical forms which are (a) fluids, (b) compounds, (c) greases, (d) resins, and (e) elastomers.

Either tetrachlorosilane, $SiCl_4$ or tetraethoxysilane, $(C_2H_5O)_4Si$, both of which are liquids, can be used as a starting material for the attachment of the organic groups directly to the silicon atom in the synthesis of silicones. This can be done by replacing one or more of the Cl atoms of $SiCl_4$ or of the corresponding ethoxy groups of tetraethoxysilane with an organic group (R) by the Grignard reaction.

Cellulose Ether Wax

An alkyl ether of cellulose, as typified by *ethylcellulose*, may be incorporated or used with waxes to obtain wax compounds of considerable value in the arts. The properties depend primarily upon the degree to which the cellulose has been etherified. According to Koch[11] it is customary to consider the cellulose molecule as composed of glucose residues, each of which has three hydroxyl (OH) groups available for etherification. The commercial product, with 47 to 48 per cent ethoxy content, has the equivalent of about 2.4–2.5 hydroxyl groups etherified, has about the lowest incipient softening point, and possesses optimum solubility in polar and nonpolar solvents.

Ethylcellulose possesses remarkable thermoplastic properties, and wide use of this important characteristic is possible because it is also stable to heat. It has low flammability, is transparent to light, does not discolor by sunlight, is inert to alkalies and to dilute acids, and is compatible with a great variety of waxes, resins, and plasticizers. Ethyl cellulose materially

toughens, hardens, and raises the melting point of the materials with which it is compatible.

Ethylcellulose is not miscible directly with ceresin, ozocerite, or paraffin wax. It is compatible with montan wax, esparto wax, beeswax, candelilla wax, japanwax, spermaceti, stearic acid, and with waxy aliphatic alcohols such as lauryl, cetyl, and stearyl alcohols. It has a limited compatibility with carnauba wax. Outstanding toughening action occurs when ethyl cellulose is compounded in binary mixtures with beeswax, and japanwax. If the ethylcellulose is first dissolved in a compatible wax, such as beeswax, a considerable amount of a hydrocarbon wax, such as paraffin, may be added to the solution before any evidence of incompatibility is encountered. Ethylcellulose diminishes the tendency of waxes to crystallize and decreases the shrinkage, strikingly so in the case of mixtures with montan wax.

The effect of ethylcellulose addition on the melting point of waxes has been tabulated by Koch[11]:

Composition (Per Cent)		Drop Melting Point (°C)			
Wax	Ethylcellulose	Purified Montan Wax	Bleached Beeswax	Stearic Acid	Refined Coal Tar
100		69.5	62.5	55.0	27.5
90	10	86.5	103.5	56.0	88.0
75	25	115.0	144.0	71.0	118.0
66.7	33.3	117.5	—	87.0	132.0
50	50	134.5	182.0	114.0	171.0

In ethylcellulose mixtures it is customary to use a small amount of plasticizer, usually 15 per cent or less by weight, based on the ethylcellulose content. Ethylcellulose is compatible with most plasticizers; it is also compatible with many resins, such as rosin, hydrogenated rosin, ester gum, modified phenolic resins, dewaxed dammar, etc. It is incompatible with urea-formaldehyde resins, hydrocarbon resins, vinyl resins, polystyrene resins, high-melting coumarone resins, and some others. However, modifying agents which are good mutual solvents for both the ethylcellulose and the incompatible resin, greatly improve the tolerance of ethylcellulose for many incompatible resins.

When beeswax is heated considerably above its melting temperature, with efficient mechanical stirring, somewhat over 25 per cent of ethylcellulose can be incorporated. Lower amounts of ethylcellulose such as 5 or 10 per cent are more readily dissolved, that is, dispersed. The *cellulose ether waxes* are noncrystallizable, smooth in texture, and high in melting point, but their high viscosity limits the breadth of industrial application. Coating compositions made up of resins, plasticizers, and waxes are often improved in homogeneity, smoothness, tensile strength, and chemical resistance by

incorporating ethylcellulose in such compositions. Compositions of this sort are very thermoplastic, and can be manipulated as molten mixtures at elevated temperatures. They form the bases for heat-sealing adhesives, coatings, and laminants of metal foil to paper. When pigmented with colors they are of value for cheap casting plastics, crayons, pastels, and the like.

Kropscott Process. The inclusion of wax in cellulose ethers, such as ethylcellulose, to facilitate the extrusion for cable coverings, wire insulation, etc., may be conducted by the Kropscott process[12]. In the process the wax is melted in hot water and dispersed by vigorous agitation. An emulsion of the cellulose ether is then added to the agitated molten wax dispersion. The solvent contained in the emulsion can be driven off with the aid of steam, whence the cellulose ether precipitates and immediately absorbs the wax to form uniform granules. After cooling, the granules are removed and dried in an oven or in a shelf drier. The process, according to Kropscott, can also be modified so that either water-wet cellulose ether, or dry cellulose ether dispersed in alcohol and water, is agitated with pulverized wax. The object of the Kropscott process is to secure upon the removal of the solvent a free-flowing granular particle of wax containing cellulose ether.

Montan, paraffin, candelilla, carnauba, esparto waxes, "Castor-wax," petroleum ceresin, stearamide, or mixtures of two or more of these substances may be used as the wax foundation for the cellulose ether waxes. Hydrogenated castor oil is particularly useful for the purpose. The cellulose ethers may be methyl, propyl, butyl, methyl propyl, ethyl propyl, or benzyl. However, ethylcellulose is generally employed. Kropscott has given the properties of granular ethyl cellulose compositions comprising wax, rating them on the basis of ethoxy content.

(4) "REPLACEMENT" AND SUBSTITUTE WAXES

The word "replacement" as applied to waxes is a term which has found its way into the literature on waxes and is perhaps deserving of mention. A "replacement wax" is a substitute for a well-known wax when the latter is no longer available, or obtainable only at a prohibitive price. The shortage of natural waxes and other commodities in World War II created the need for "replacements," or so-called "ersatz" material. For example, a replacement for beeswax or beeswax substitute might be formulated from *beeswax* 10, *montan wax* 2, *stearic acid* 0.3, *spermaceti* 5.0, *carnauba wax* 1.5, and *ceresin* 1.2 parts. Microcrystalline waxes, off-specification in quality from the Government designated grade, were offered during World War II under the name of "Victory Wax," etc.

Glickman[3] attempted to distinguish between "substitute" and "replacements." He defines a substitute as a compound which may be directly utilized in lieu of the original compound (wax) without requiring any modi-

fication of the formulation or procedure in order to obtain an equivalent finished commercial product. For example, in India a substitute for carnauba wax in the manufacture of carbon paper is prepared by melting together *lac wax* (85 parts) with *beeswax* (10 parts), heating to 210–230°C, gradually adding 5 parts of "India sal resin," straining, and cooling, to give a hard, lustrous, waxlike compound. India sal resin is the dammar-like exudate of *Shorea robusta* Gaertner, commonly known as the salshorea, or sal tree. Puntambekar[13] gives the properties of this carnauba substitute as: density (d^{15}) 0.993, melting point 83°C, acid value 6.3, and saponification number 85.6, and states that it complies with the specifications for carnauba wax.

Glickman[8] defined a "replacement" as a material which may be used in place of the original wax, but which requires some modification in formulation and/or processing to achieve results equivalent to those obtained with the natural product. "Replacement waxes" have appeared on the market which imitate the properties of beeswax, japanwax, carnauba wax, and bleached montan wax. These replacements are offered under various trade names; e.g., the "Beacon" line of waxes is of this order.

Corkery[6] prepared an imitation of carnauba wax by combining a glyceride (C_{16}, C_{18} or like) with a coumarone indene resin (m. 100°C) soluble in mineral spirits. He found that he could combine the stearin and/or palmitin with the resin in proportions approximating 2:3 or 3:2. A *carnauba replacement wax* offered in the market but of a nondescript origin proved to have the following properties: specific gravity (d_{15}^{15}) 0.995, melting point 76–77°C, acid value 14.8, saponification number 88.6, ester value 73.8, and iodine number (Hanus) 38.7. Both the acid value and iodine number are higher than those found in carnauba wax. It is very hard, of a dark brown color, and resembles carnauba except for color.

A "replacement wax" for carnauba has also been made by melting together *behenone*, $(C_{21}H_{43})_2CO$, which is a waxy ketone, and *hardened castor oil* in the proportion of 20:80. The finished wax is high in melting point and hardness. In general, glycol or glyceryl esters of 12-hydroxystearic acid may be reacted with keto or hydroxy compounds of the fatty acids having a melting point below 70°C. Another replacement for carnauba has been made by cooking or saponifying fatty oils with calcium hydrate, and mixing the reaction products with *candelilla wax*. The replacement is said to be of value in wood, metal, or leather polishes.

References

1. Abrams, A., Forcey, G. W., and Wagner, C. L., U. S. Patent 2,275,814 (1942).
2. Allan, R. W., *Chem. Ind.*, **42**, 501 (1936).
3. Auer, L., U. S. Patent 2,406,336 (1946).
4. Butler, J. M., U. S. Patent 2,580,996 (1952).

5. Canada Paper Co., and Szwarc, A., Canadian Patent 479,085 (1952).
6. Corkery, F. W., U. S. Patent 2,255,242 (1941).
7. Gebauer-Fuelnegg, E., *et al.* (Marbon Corp.). U. S. Patent 2,255,564 (1941).
8. Glickman, C. S., *Chem. Ind.*, **53**, 4, 496 (1943).
9. Humes, W. S., U. S. Patent 2,361,477 (1944).
10. Imperial Chemical Industries, Ltd., British Patent 546,862 (1942).
11. Koch, William, *Ind. Eng. Chem.*, **29**, 687–690 (1937).
12. Kropscott, E. L., U. S. Patent 2,241,706 (1941).
13. Putambekar, S. V., *Forest Research Inst., Dehra Dun, Indian Forest Leaflet*, **19**, 3 pp. (1942).
14. Schneider, H. G., Young, D. W., and Rocca, J. P., U. S. Patent 2,577,624 (1951).
15. Scripture, Jr., E. W., U. S. Patent 2,275,272 (1942).
16. Snyder, J. E. (to Wingfoot Corp.), U. S. Patents 2,307,081 and 2,308,180 (1943).
17. Sparks, W. J., U. S. Patent 2,339,958 (1944).
18. Thies, H. R., *Rubber Age (N. Y.)*, **45**, 17–21 (1939); *Paper Trade J.*, **108**, No. 8 96–102 (1939).
19. Thomas, G. C. (to The Lummus Company), U. S. Patent 2,290,393 (1942).
20. Warp, H., U. S. Patent 2,141,575 (1939).

8. Emulsifiable Waxes, Waxy Alcohols and Acids, Metallic Soaps, Wax Emulsions

EMULSIFIABLE WAXES AND WAX STOCKS

An emulsion is a two-phase system, consisting of two incompletely miscible liquids, the one being *dispersed* as finite globules in the other. The dispersed (internal) phase is the liquid that is broken up into globules. The surrounding liquid is known as the *continuous* (external) phase. A *suspension* is a two-phase system closely related to an emulsion, in which the dispersed phase is a solid. An *emulsifying agent* (emulsifier) is a material usually added to one of the phases to facilitate formation and stability of the dispersion.

In *oil-in-water* (*O/W*) *emulsions*, the oil is dispersed in water, the continuous phase. In *water-in-oil* (*W/O*) *emulsions* water is dispersed in oil, which is the external phase. An O/W emulsion may be diluted with water, whereas a W/O emulsion may be diluted with oil. Properties of emulsions involve dispersibility, viscosity, stability, particle size, particle-size distribution, electrical conductivity, and ease of formation.

Emulsifiers (emulsifying agents) are presently considered a subdivision of the general class of *surface-active agents*, which latter include wetting agents, solubilizers, detergents, suspending agents, etc. (see Surface-Active Agents, p. 539). Emulsifiers may be divided into *ionic* and *nonionic* types. The ionic type is composed of an ordinary lipophilic (oil-loving) group and a hydrophilic (water-loving) group. In sodium stearate the surface-active fatty acid portion represents the anion of the molecule, and the soap is classed as an *anionic* emulsifier (see p. 540). This is also true of morpholine oleate, sodium oleic acid sulfonate, sodium castor oil sulfonate, lithium stearate, aluminum stearate, and magnesium oleate. Examples of nonionic emulsifiers are polyglycol fatty acid esters, polyoxyethylene fatty aclohol ethers, lecithin, cholesterol esters, lanolin, and the like. Quaternary ammonium salts are classed as *cationic* emulsifiers, as are also the amine hydrochlorides.

Emulsifiable Waxes

An emulsifiable wax is a wax which can be dispersed (suspended) in water, with or without alteration of its chemical composition. Waxes which contain free alcohols and free acids are emulsifiable but usually require the assistance of a dispersing agent. Since most of the natural waxes have a low content of either free alcohols or free acids, but are largely constituted of alcohol-esters and a varying proportion of hydrocarbons, preference is given to substitutes or synthetic waxes which are expressly made for emulsification purposes.

In the emulsification of natural wax use is made of the fact that a portion of the wax is saponifiable with boiling alkaline solutions; for example, *beeswax* can be emulsified to an appreciable extent by saponifying it with dilute sodium hydroxide solution. Saponified natural waxes in most instances can be replaced in part or as a whole by substitutes such as a combination of sodium castor oil sulfonate (Turkey red oil), fatty acids of high melting point, and high-melting hydrocarbon waxes. Such mixtures emulsify easily with warm water. Resins are also used in place of fatty acids, with alkaline oleates replacing alkaline oleic acid sulfonates. *Japanwax* mixed with about half its weight of palmitic acid can be treated with sulfuric acid (i.e., sulfonated) and then partially neutralized with ammonium hydroxide to obtain a product which is emulsifiable with water.

Included in the emulsifiable synthetic waxes of a nonionic type are certain esters of polyhydric alcohols and fatty acids of high molecular weight. These emulsifying waxes themselves become powerful emulsifying agents for other waxes, by the addition of alkali or other suitable surface-active compounds. Emulsifying waxes are also modified chemically so that they become self-emulsifying and ready for use in compounding polishes and the like.

Some of the emulsifiable prepared or synthetic waxes which have appeared in the world market are "Lanette Wax," and a series of "Abril Waxes," both produced in Great Britain; "Haftax Wax" (von Heyden A.G.); "Karawax" (K. Himmelbauer, M. Ostrafa, CS.R.); "Gersthofen Wax E" (Werk Lech-Chemie Gersthofen), and "Glycol Waxes" produced in the United States. The latter waxes consist generally of fatty alcohols and/or polyhydric alcohols more or less combined with the higher fatty acids (see p. 534).

Waxes with Free Alcohols. Typical of an emulsifiable wax which contains free alcohols is "*Lanette Wax*" (m. 50°C) the composition of which is substantially a mixture of cetyl and stearyl alcohols, which have been sulfated or phosphated to some extent to make the alcohols hydrophilic and emulsifiable. "Lanette Wax" is soluble in ethanol, ether, benzene, and

many other solvents. Its greatest utilization in the arts is in the emulsification of water-base compounds—those containing soap—and sulfonated animal, vegetable, or mineral oils. "Lanette Wax" is used in conjunction with pentamethylene glycol in the preparation of facial creams.

"*Rilan Wax*," like "Lanette Wax," is used in emulsions for leather dressings, etc. "*Karawax*," which consists of wax alcohols and free fatty acids, is readily emulsifiable, lending itself to the manufacture of liquid shoe and furniture polishes. It has a specific gravity (d^{15}) of 0.950–0.955, melts at 67–70°C, has an acid value of 17–22, and a saponification number of 44–50.

Hydrocarbon-Wax Emulsions

The stability of a wax emulsion containing hydrocarbons is dependent upon the size of the particles of colloidal dimensions: the smaller the size in A units the more persistent is the stability. The particle size is influenced by the mean molecular weight of the hydrocarbons used in the particular formulation. Kerosene may be used in considerable proportion in natural or synthetic wax emulsions of the W/O type because of the relatively low molecular weight of its hydrocarbons.

Slack wax is also usable in large proportion, whereas *refined paraffin* or *microcrystalline waxes* of high melting points would only be employed in relatively small proportion, when used as the chief source of hydrocarbons, in emulsions prepared from natural or synthetic waxes, emulsifying agent, and resin. When preparing emulsions of the natural plant waxes, or the synthetic high molecular weight alcohols such as "*Lanette Wax*," the allowable amount of ordinary refined paraffin wax is about 25 to 50 per cent of the total mixture. Less hydrocarbons would be used with *candelilla* than with *carnauba wax*, since the former contains 50 per cent of natural hydrocarbons.

Emulsifiable wax products are marketed which provide a foundation for polishes, etc. (see following section, Emulsifiable Wax Stocks).

Emulsifiable Wax Stocks

The term "emulsifiable wax stock" applies to a wax preparation, conveniently in a form that is water-free or nearly so, and which can be very readily emulsified with water. There are innumerable preparations of this kind on the market for use in compounding polishes, pastes, and leather dressings, for waterproofing paper, etc.

Emulsifiable wax stocks of the anionic type may be made from *scale wax* (m. 120–124°F) 88 parts, and petroleum sulfonate (50 per cent) 12 parts; from *paraffin wax* (m. 128–132°F) 90 parts, petroleum sulfonate (50 per cent) 5 parts, and water 5 parts; also from other combinations of similar material. Such an emulsified wax stock when dispersed in water to give an

emulsion containing about 5 per cent of wax, according to Griesinger[17] may be successfully employed in waterproofing paper and cardboard.

For use in the paper beater the emulsifiable wax stock may be prepared from *crude yellow scale wax* 85 parts, petroleum sulfonate (50 per cent) 15 parts, admixed with a sufficient amount of water to give a 5 per cent wax emulsion. (Also see Scale Wax Emulsions.)

The principle involved in preparing many of the commercial wax preparations such as metal polishes, stove polishes, pastes, abrasive soaps, polishing creams, etc., is to effect an emulsifying wax combination from hydrocarbons with high molecular weight alcohols (waxy alcohols), together with a high carboxylic or resin acid; the mixture is emulsified with the aid of a dilute alkali. The hydrocarbons can be selected from a group consisting of *paraffine, ceresin, ozocerite,* or the like; the alcohols from a group comprising *woolwax alcohols, cetyl alcohol,* and *mono-* or *diglycerides*; and the acids from stearic, palmitic, etc., or colophony. The alkali is often none other than sodium carbonate, but for many purposes the ethanolamines are preferred. *Spermaceti* may be effectively used instead of the alcohols.

Miscellaneous Emulsifiable Wax Stocks. Noncle[22] formulated an emulsifiable wax stock from *candelilla wax, shellac wax, lignite wax,* stearic acid, and zinc stearate. For making W/O polishes the wax stock is then emulsified with a white mineral spirit containing a little ammonia or an amine, and a mild abrasive is added. Insecticide spray emulsions for plants are of the anionic type, and the stearic acid ingredient is said to require a very low iodine number (less than 0.5) in order to prevent leaves from browning.

"*Seycowax*" (product of Seydel-Woolley & Co.) is a special softening and lubricating wax for textiles, generally used in conjunction with warp-sizing compounds.

Friedrich[16] treated woolwax (anhydrous lanolin) with metallic sodium for one hour at 150°C and obtained an emulsifiable wax-like product. Unsaturated waxes treated with a sulfite and an oxidizing agent, air or oxygen, without the addition of acid, are said to yield water-soluble products. Belt dressings of O/W emulsion type can be made with rosin in combination with *woolwax, montan wax,* or other emulsifiable wax.

Emulsification Equipment

Emulsification equipment must necessarily be of simple design and portable if used in the field. In the laboratory it may consist of a high-speed blender, gyroblend shaker, motor-driven egg beater, etc. A high-speed blender consists of a stainless steel container with a capacity of 5 quarts or less, with sharp stainless steel blades whirling as fast as 16,000 rpm. Al-

though wrist-action mixing might suffice to produce an emulsion, this same principle of rapid blending action is more effectively accomplished by the gyroblend bottle shaker, which provides up to 750 shakes per minute, and may be equipped with an automatic timer to allow intermittent or continuous operation. The laboratory also often uses one or more types of pilot plant models of motor-driven propellers, turbines, colloidal mills, and homogenizers.

In plant manufacturing operations, slow-speed equipment for emulsification, such as pebble and ball mills, is suitable for a strictly limited number of emulsions. The mechanically rotated paddle or anchor type agitator is frequently used. High-viscosity emulsions in the food industry are prepared with the planetary stirrer. Propeller agitation is suited to low- and medium-viscosity emulsions, whereas turbine-type agitators are suited to high viscosities. Colloidal mills are used where a very high shearing force is needed, although a still finer but less uniform particle is given by the homogenizer. A more recent development for emulsions of low-viscosity liquid is the high-frequency or ultrasonic oscillator.

Scale Wax Emulsions

Emulsifiable wax products may be made from *scale wax* (m. 120–124°F) 88 parts, and petroleum sulfonate (95 per cent) 12 parts; from *scale wax* 88, and petroleum sulfonate (50 per cent) 12 parts; and from *paraffine* (m. 128° to 132°F) 90, petroleum sulfonate (50 per cent), 5, and water 5 parts; also from other combinations of similar material. Such emulsifiable wax stocks when dispersed in water to give an emulsion containing about 5 per cent wax, may be successfully employed in waterproofing paper and cardboard, according to Griesinger[17]. For use in the paper beater the emulsifiable wax stock may be prepared from crude yellow scale wax 85 parts, sulfonate (50 per cent) 15 parts, admixed with a sufficient amount of water to give a 5 per cent wax emulsion. This emulsion is added to the pulp in the beater so that there are 3 pounds of wax to 100 of pulp. The addition of alum solution breaks the emulsion and causes the wax to deposit upon the paper fibers. When the paper is sheeted it will have a low water adsorption power, about 25 to 30 per cent. Paper of this sort has been used in packaging milk and other food products.

Oxidized Hydrocarbon Waxes

Hydrocarbon waxes, such as paraffin and microcrystalline waxes, which have been artificially oxidized to produce an appreciable amount of fatty acids, or saponifiable matter, are known as *oxidized waxes*. The object of oxidizing hydrocarbon waxes is to make them more or less saponifiable. The oxidation is accomplished by blowing air through the molten wax for

a prescribed period of time at a controlled temperature. In carrying out the oxidation of paraffin waxes (m.p. 52–57°C) the temperature should range between 150 and 180°C; the application of increased pressure speeds up the reaction when air is used as the oxidizing agent. By withdrawing the partially oxidized wax and adding fresh wax to the reaction zone the darkening of the oxidized product can be avoided.

The wax acids produced in the oxidation process of both fatty and hydroxy acids as well as their anhydrides, lactones, and lactides, give oxidized waxes their peculiar characteristics. The hydroxy acids are in the range $C_{13\text{-}17}H_{26\text{-}34}OH \cdot COOH$. Catalysts of manganese, nickel, chromium, and cobalt can be resorted to, when it is desired to obtain a higher yield of acids in the oxidized wax.

The Warwick Wax Company was first to produce oxidized microcrystalline (OMC) waxes, at Chanute, Kansas, in 1945. About 1947, Petrolite Corporation, Ltd., at Kilgore, Texas was the second to produce OMC waxes. A third producer is the Bareco Oil Company, Tulsa, Oklahoma.

The oxidized waxes are graded commercially by melting point, by acid number (neutralization number) and a so-called "minimum" saponification number or value, a basis on which they are also priced. Microcrystalline waxes are similarly oxidized to the paraffins for commercial utility. Specifications for OMC waxes of the Warwick Wax Company follow:

A specimen of OMC wax labeled "Melting point 84°C minimum, saponification number 80, acid value 16.5, penetration 3–5, price 38¢ per lb. f.o.b. New York" had the following characteristics: pale yellow; very firm but unctuous feel; slightly fatty odor; melting point (drip) 88.5°C (191°F); softening point (Ring-and-Ball) 85°C, (Ring-and-Plunger) 70°C; Fisher-Johns melting point 70° minimum, 88°C maximum; penetration (100 g/25°C/5 sec) reading 5; durometer hardness 93 at 25°C. A specimen of OMC wax from another source had a melting point of 180–185°F, penetration (100 g/25°C) 6–7, and a color rating of 3 NPA. Its acid value was 22–28, and saponification number 50–60. It had a Saybolt viscosity of 130 maximum at 210°F. It was priced at 33½¢ per lb.

OMC waxes offered by Warwick Wax Company under the trade name "Cardis" are given below. They are here listed in their order of hardness as determined by penetrometer.

Name of Wax	Melting Point (°F) ASTM D-127-30	Penetration 100 g/77°F/5 sec	Color NPA	Acid Value	Saponification Number
"Cardis 1"	195–200	1–2	(orange-brown)	—	—
"Cardis 314"	184–189	4–6	4–5	13–15	45–50
"Cardis 262"	195–200	4–6	(brown)	14–16	40–45
"Cardis 319"	180–185	5–7	4½–6	18–20	65–70
"Cardis 320"	180–185	5–7	4–5	28–30	75–80

"Petronauba Waxes" are emulsifiable waxes developed by Bareco Oil Company (Tulsa, Oklahoma); they are made by the oxidation of high molecular weight microcrystalline wax. *"Petronauba C Wax"* has a melting point of 180°F (min.), penetration (100 g/5 sec/77°F) 3 (max.), color NPA 3 (max.), acid number 22–28, saponification number 50–60, and viscosity (SSU at 210°F) 130 seconds.

Uses of OMC Waxes. Oxidized microcrystalline waxes are of particular value in the preparation of wax emulsions, such as liquid softening, lubricating, and polishing agents. The melting point and hardness of the source of the raw material, pure hydrocarbons, are well maintained in the corresponding oxidized wax, but the softening point, owing to the presence of low melting point, chemically altered constituents, will have greatly decreased after the oxidation treatment.

It is the unctuous fatty acid constituent in an otherwise hard wax that makes the oxidized wax a valuable adjunct in compounding waxes to suit requirements where such properties are needed, as in certain carbon paper, marking crayon, and polish formulations.

In some of the dry-bright, rubless floor polish formulations, "Durez" resin (Durez Plastics and Chemicals, Inc., North Tonawanda, N. Y.), "Shanco" resin (William H. Scheel, Inc., Brooklyn, N. Y.), "Shelite" resin (T. F. Washburn, Inc., Chicago, Ill.) and carnauba wax are used in conjunction with the OMC wax. Formula evaluations of such resins with "Petronauba Wax" have been made by the Bareco Oil Company.

A potential maximum close to 10,000,000 pounds of OMC waxes has been estimated as a requirement of the polish industry, which in 1950 imported 30,000,000 pounds of hard waxes, of which a little over 20,000,000 pounds was carnauba wax. The cost of the OMC waxes was 34–40¢ per lb, and of carnauba, $1.20 per lb, in 1952. Ninety per cent of the 1952 production of OMC waxes went into no-rub floor polishes.

Emulsifying Agents or Emulsifiers

There is a group of emulsifying agents known as the *amine soaps*, which are of great importance in the preparation of emulsifiable wax stocks and technical emulsions. The amine soaps are formed by the reaction of an amine, such as triethanolamine, $N(CH_2CH_2OH)_3$, with fatty acid in theoretical combining proportions. With the liquid acids, such as oleic, or cocoanut fatty acids, the preparation of the amine soap may be conducted at room temperature; with the solid acids, such as stearic acid, it is necessary to melt the fatty acid and the amine (about 1:2) together before the reaction will form the amine soap. Emulsions prepared with amine soaps are distinguished by their ease of preparation, small particle size, noncorrosiveness, stability in storage, low alkalinity of their water solutions,

and detergent power. Triethanolamine is a viscous liquid with slight ammoniacal odor, very hygroscopic, soluble in water, miscible with polar solvents such as alcohol, but insoluble in nonpolar solvents such as gasoline and benzene. It is not harmful to textiles nor caustic to the skin.

Triethanolamine stearate (T.E.S.) is a hard, white product that changes to a tan color on aging. It is widely used in the preparation of cosmetics and pharmacals. The following recipes show how T.E.S. is employed in O/W emulsion: (1) *Eucalyptus oil emulsion*: eucalyptus oil, 75, water 85, and T.E.S. 14 parts. (2) *Paraffin wax emulsion*: paraffin wax 85, water 200, and T.E.S. 10 parts. The oil, or wax and the T.E.S. are melted together, and the water, which has been previously warmed, is added slowly with rapid agitation, and the stirring continued until the preparation cools.

Monoethanolamine stearate, the fatty acid ester from monoethanolamine, $NH_2(CH_2CH_2OH)$, and stearic acid, is soluble in hydrocarbon solvents and in mineral oils, and the W/O emulsion is an excellent cleaning agent. *Isopropanolamine stearate* in the technical grade is a mixture of the fatty acid esters of mono-, di-, and triisopropanolamine, and its preferred use is where it is necessary to hold the white color of cosmetic emulsions permanently.

Morpholine soaps are prepared from morpholine, which is an amine of the formula $O \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2$. Morpholine has a higher boiling point (128°C) than other amines, and is used where it is advantageous to boil the dilute water solutions, or where the dried emulsion film of soap is to have wear resistance. Other amine emulsifiers of anionic type include those prepared from diethylethanolamine, a hygroscopic liquid which gives fatty acid esters useful in making acid wax emulsions such as those of suspended aluminum formate in water and beeswax which are stable when diluted to 5 per cent wax content.

Ammonium laurate, a tan-colored soft solid, is an excellent emulsifying agent, particularly for the production of O/W emulsions with a high oil content, e.g., mineral oil 65, ammonium laurate, 2, and water 10 parts. The oil is warmed and added slowly to the laurate water dispersion, with constant stirring until cool.

Ammonium stearate is a somewhat waxy solid which can be dispersed in boiling water to form a stable white paste, or fluid emulsion, by stirring while cooling. The combined stearic acid content of ammonium stearate is 94.3 per cent, but increases with the loss of ammonia on exposure to air. It is preferable to sodium and potassium stearates for emulsions, and is of value in waterproofing cements, cold water paints, stucco and concrete. In preparing the cement for use, a dispersion is first made of the stearate in water (1:3) and one half gallon of the paste added to a bag of dry cement, mixing in the premeasured amount of water. A little ammonia water can be added to increase the speed of setting.

Ammonium stearate is used in cosmetics, i.e., in the manufacture of vanishing creams, brushless shaving creams, and similar products. It is used in paste form in the preparation of water-repellent coatings for paper, textiles, and rubber. When dispersed in water it can be applied by spray, brush, or dip method. On drying, the water and ammonia are drawn off, leaving a water-repellent film.

Ammonium linoleate, a solid which completely melts to a reddish liquid at 75°C, is an excellent emulsifying agent. Dutton[9] has described its value in the preparation of a tree wax emulsion that is effective in protecting living trees from sunscald, borer, and fungus injury. The emulsion may be prepared from ammonium linoleate (dissolved in 50 parts of hot water) 3 parts, bentonite (smoothly dispersed in 50 parts of water) 3 parts, paraffin wax 10 parts. The ammonium linoleate solution and the bentonite dispersion are mixed at 70 to 90°C, and the molten paraffin slowly poured into the hot mixture; the resulting slurry is vigorously stirred until a good emulsion is obtained. When cooled the product is creamy. A recipe for spraying is given as: stock emulsion 36, water 36, aluminum powder 7.2, water to complete 44 parts. Waxes other than paraffin may be used in making the stock emulsion.

Ammonium acid soaps are also used to emulsify oils and waxes. These soaps are *ammonium caprylate*, acid (m. 70°C), the *laurate* (m. 80°C), *myristate* (m. 75–90°C), *palmitate* (m. 100°C), and *stearate* (m. 100°C decomposes). The ammonium acid soaps have the general composition,

$$NH_4 \cdot C_nH_{2n-1}O_2 \cdot C_nH_{2n}O_2 ,$$

where n denotes the number of carbon atoms in the fatty acid. E.g., *ammonium myristate, acid* has the formula $NH_4 \cdot C_{14}H_{27}O_2 \cdot C_{14}H_{28}O_2$.

Petroleum sulfonic acid is finding an important use in the preparation of wax emulsion stocks for waterproofing paper, cardboard, leather, and textile material. The *petroleum sulfonates* employed are oil-soluble sodium salts of sulfonic acids derived in the manufacture of white mineral oil by the sulfuric acid treatment, the sulfonic acids having an acid value of 119 mg KOH per gram. The preparation of the emulsion stock has been described by Griesinger[17]. The ingredients are in the nature of scale wax, which is melted at 200°F together with refined paraffin wax; 3 to 12 per cent of sulfonate soap is added, and the admixture mechanically agitated while hot. The stock may be formed into cakes, sticks, granules, pellets, flakes, or the like, depending upon the requirements of the user. The emulsifiable stock is diluted with water so that it contains no more than 5 per cent of wax when added to the paper pulp beater.

When waterproofing paper stock with the sulfonate emulsion, a sufficient quantity of electrolyte such as alum solution is added to break the emulsion

and precipitate the wax upon the paper fibers. After sufficient beating the pulp is delivered to the sheet fabricating machine in the ordinary way. Closely related is the previous discovery that emulsions of waxes for the treatment of fibers or fibrous material may be readily brought about by the use of *amylated naphthalene-sulfonic acid* or *hexalated naphthalene sulfonic acid.*

Synthetic Emulsifiable Waxes

Natural or synthetic waxes of the ester type are heated to not exceeding 200°C with a nitrogenous base containing one or more nitrogen atoms and a nickel or cobalt catalyst; the properties of the wax may then be modified by treatment with substituted alkylene oxides such as ethylene oxide, or with epichlorhydrin, etc. The resulting products are useful as soap substitutes, as assistants in the treatment of chemicals, and as anionic emulsifying agents for oils. For example, (1) *beeswax* is heated to 150–160°C with ammonia to give a product useful as an ingredient in polishes containing wax; (2) *sperm oil* is heated to 140–150°C with ethanolamine containing a little water in paraffin hydrocarbons to form salves; (3) *woolwax* is heated to 160–170°C with ethanolamine containing a little water—a product useful for preparing oleic acid emulsions is obtained by treating the product with ethylene oxide at 60–70°C in the presence of aqueous alkali.

The I.G. Farbenindustrie A.G. held a British patent[22] for separating components, i.e. hydrocarbons, acids, and alcohols, from waxes such as beeswax, montan wax, and woolwax. The method consists of saponifying the wax, atomizing the saponified product to convert it into a dry powder, extracting the powder with solvent, and acidifying the soaps. It is claimed that the method constitutes a step in the further synthesis of waxes of a superior order.

The emulsifiable types of polyethylene waxes differ from the regular types in having free acid groups which are preferably built into the polymer molecule. They form stable clear emulsions easily prepared, even in formulations of high solids content. They find trade applications in floor waxes, shoe polishes, and in coatings of various types in the asbestos shingle, paper, and textile industries. The commercial grades of emulsifiable polyethylenes are exemplified by *"AC-Polyethylenes" 629* and *729* (Semet-Solvay Petrochemical Division, New York), and *"Epolene E"* (Eastman Chemical Products, Inc., Kingsport, Tennessee). The commercial types come within the following specifications: melting point 95–102°C (208–215°F); penetration hardness (tenths of mm 100 g/5 sec/77°F) >1–2.0; acid number 9–17; saponification number 9–17. One of two methods is used in preparing the emulsion, that is, either the "wax to water" or "water to wax" technique. The former is favored when the emulsifiable polyethylene is to be pre-

blended with lower melting waxes. Without the latter the emulsion proportions are: emulsifiable polyethylene 30, oleic acid 6, morpholine 6, and water 138 parts. Experimental grades of higher acid number, and of beeswax consistency are said to have outstanding action in improving the dispersion of nonemulsifiable waxes.

Several types of *"Gersthofen Waxes"* (also see p. 462) are emulsifiable. *"Gersthofen Wax E"* has outstanding emulsification properties. In practical use it is often blended with other Gersthofen types. Emulsions can be made with "Wax E" that are remarkably smooth and produce polishes of high luster and permanency. *"Gersthofen Wax KPS"* is used with or without carnauba wax, "Durez 219" resin, "Polyethylene AC-629," and shellac in preparing dry bright emulsions. The saponifying agent is oleic acid and morpholine, with the addition of sodium borate if either polyethylene or shellac is employed.

"Duroxon Waxes" (Dura Commodities Corporation, New York) are by-products of the Fischer-Tropsch process (Krupp Kohlechemie G.m.b.H.), Germany. They range from hard to soft consistencies. They readily emulsify with water to which alkali has been added. They form stable dispersions of the O/W class so that they are of value in preparing lubricating greases. "Duroxon D 250" has a solidification point of 45–50°C, an acid value of 110–130, and a saponification number of 225–260, and contains 25–30 per cent of unsaponifiables.

Polyhydric Alcohol Fatty Acid Esters

Among the ester emulsifiers of prime importance are the monoglycerides, since there are two hydroxyl (OH) groups in the glyceride available for *hydrophilic* (water-loving) function while the fatty acid esterified to the third OH group becomes the *lipophile* (oil-loving factor). The first of these emulsifiers was *glyceryl monostearate*, but there are now also commercially available the oleate, myristate, laurate, and palmitate. The new agencies include propylene glycol esters as well as esters of sorbitan and polyethylene glycols. The sorbitan esters in addition may be polyethylated, increasing the size of the hydrophile to any desired size.[20]

These ester emulsifiers are waxlike bodies. *Glycol monopalmitate* and *glycol monostearate* are insoluble in water, and quite soluble in alcohol. *Glycol dilaurate* (m. 50–52°C), and *glycol distearate* (m. 76–77°C) are insoluble in water, and but slightly soluble in alcohol. Ethylene glycol, $HOCH_2CH_2OH$ (liquid b. 197°C) is commonly called *glycol* and is a solvent for waxes.

Since propylene glycols exist as isomerides, namely α-propylene glycol, $MeCH(OH)CH_2OH$, and β-propylene glycol, $CH_2(CH_2OH)_2$, the fatty acid esters also exist as isomerides, that is, the propylene glycol esters and the

trimethylene glycol esters. Howe[21], at McGill University, prepared such esters in a pure state from glycols and acids of known purity. A charge of glycol and acid was esterified at constant temperature for several hours in an electric oven, the mixture being under constant stirring with a platinum stirrer electrically driven.

The hard cake of waxy solid thus obtained was melted and washed with water to remove the excess glycol. The uncombined acid present in a certain amount of this mixture was extracted and a calculated amount of sodium bicarbonate added to the batch to neutralize the free acid. The water-washed mixture was then fused in a porcelain dish on a water bath for one hour. The ester was washed out with hot ethyl ether using a hot filter. This was allowed to crystallize at room temperature, filtered, and the residue dissolved in ethanol (95%) and crystallized at about 0°C. A series of fractional crystallizations was made until the mono- and diesters were obtained pure as shown by their constant melting points. In general the products crystallized out in thin shiny plates of irregular outline, often in rose-like masses. Howe[21] has given the melting points, refractive indices, and solubilities in ethanol at two temperatures of eleven of these compounds. Solubilities were determined as grams solute per 100 grams of absolute ethanol.

Ester	Melting Point (°C)	Refractive Index	Solubility in C_2H_5OH (0°C)	(15°C)
	Ethylene glycol:			
Monostearate	58.5	1.4310	0.670	2.000
Distearate	75.0	1.4385	0.010	0.020
Monopalmitate	51.5	1.4411	1.620	10.000
Dipalmitate	68.7	1.4378	0.018	0.055
	Propylene glycol:			
Monostearate	59.5	1.4424	0.0211	0.0340
Distearate	76.5	1.4366	0.0012	0.0063
Monopalmitate	54.3	1.4405	0.0193	0.0907
Dipalmitate	68.8	1.4364	0.0052	0.0115
	Trimethylene glycol:			
Monostearate	60.5	1.4437	0.0143	0.0305
Distearate	64.7	1.4397	0.0013	0.0038
Dipalmitate	56.2	1.4374	0.0244	0.0517

Diethylene glycol, $O(CH_2 \cdot CH_2OH)_2$, commonly called "diglycol," forms both mono- and diesters. These will be referred to later.

Glyceryl Fatty Acid Esters

The behavior of glycerol, $CH_2OH \cdot CHOH \cdot CH_2OH$, is similar to that of glycol. The esters in which all three OH groups are in union with the fatty acid are largely encountered in vegetable and animal oils and in fats, e.g.,

glyceryl tripalmitate (*tripalmitin*), $C_3H_5(O \cdot CO \cdot C_{15}H_{31})_3$ (m. 65.1°C), and *tristearin* (m. 70.8°C). The mono- and dihydric esters are, however, obtained artificially and are distinctly waxy bodies.

In the presence of an alkaline catalyst, either direct esterification of fatty acids or interesterification of fats provides a convenient method for preparing *monoglycerides*. The reaction product is a mixture of monoesters, diesters, and triesters as well as free glycerol, free fatty acid, and the catalyst in the form of metallic soaps. Kuhrt *et al.*[25a] have shown the pronounced difference between the composition of (a) the commercial mixtures, and (b) the molecular distilled monoglyceride products. In the following tabulation the melting points of the pure monoglycerides, e.g., glycerol-1-monolaurate (α-monolaurin), are listed as (c).

		% Monoester	% Glycerol	% FFA	M.P. (°C)
Monolaurate	(a)	35	9.5	1.2	47
	(b)	92	0.7	1.3	57
	(c)	100	0	0	63
Monopalmitate	(a)	38	3.6	2.7	61
	(b)	93	0	1.3	72
	(c)	100	0	0	77
Monostearate	(a)	40	3.9	2.3	59
	(b)	94	0.5	1.7	71
	(c)	100	0	0	81.1

Glyceryl Stearate Esters

The properties of glyceryl stearates are quite similar to those of the glycol stearates. *Glyceryl monostearate*, the official product as described in N.F. IX, is a mixture of variable proportions of glyceryl monostearate and *glyceryl monopalmitate*, and is classed as an edible solid, as contrasted to diethyleneglycol stearate. It is a white, waxlike solid or waxlike beads, or flakes, and has a melting point of 56–58°C, a saponification number 164–170, and iodine value of not more than 6. It is soluble in hot organic solvents and mineral or fixed oils, insoluble in water but may be dispersed in hot water with the aid of a small amount of soap or other suitable surface-active agent.

The commercial glyceryl monostearate, also called *monostearin*, in a one per cent aqueous dispersion shows a distinctly alkaline reaction, but it is obtainable finished to an acid condition. Monostearin usually contains an appreciable amount of *glyceryl distearate*. The products which may be made with commercial glyceryl monostearate include plasticizers, waterproofing agents, insulators, polishes, ointments, cosmetics, dental waxes, cooking oils, and fats.

Glyceryl distearate (α,α'-distearin), when prepared from the reaction product of α,α'-dichlorohydrin and sodium stearate, crystallizes in waxy

plates from chloroform. It melts at 79°C, resolidifies at 76°C, and is slightly soluble in cold alcohol but very soluble in hot alcohol. *α,α'-Dipalmitin* similarly prepared from sodium palmitate melts at 72°C. The commercial glyceryl distearate contains appreciable amounts of α-monostearin, α-monopalmitin, α,α'-dipalmitin, and other glycerides, which cause it to have a relatively low melting point (58°C optimum), and make it more dispersible in water. Glyceryl distearate is used in shortenings, oleomargarine, and other articles of food. In oleomargarine it is said to prevent the seepage of milk. It is also used as an enteric coating for pills and tablets.

Glyceryl monolaurate, or *α-monolaurin*, crystallizes in white wax-like needles (m. 63°C); α-monopalmitin in leaves (m. 77°C) which are moderately soluble in alcohol (5.306 g in 100 g at 22.4°C); and α-monostearin in needles (m. 81.1°C) which are dispersible in water. Its formula is $C_{17}H_{35}COOCH_2 \cdot CHOH \cdot CH_2OH$. If a terminal OH group is replaced by a fatty acid radical, an *alpha* ester is formed. If an adjacent group were replaced instead, a *beta* ester would result.

Commercial Polyalcohol Esters

The commercial glycol and glyceryl esters comprise glycol mono- and distearates, diglycol stearate, glycol monolaurate (m. 27.5°C), glyceryl monostearate (m. 56–59°C), glyceryl monolaurate (m. 45–46°C), diglycol monolaurate, propylene glycol stearate (m. 44°C), propyleneglycol laurate (m. 14°), and possibly a few others. The laurates are either liquids or soft solids; they are manufactured by esterifying the lauric acid obtained by hydrolysis of coconut oil with c.p. glycol. Most of the laurates are faintly alkaline, but *diethyleneglycol monolaurate* as commercially prepared is slightly acid.

Diethyleneglycol monostearate, the technical grade of which is referred to as "Diglycol Stearate S" (m. 56–57°C), is dispersible in water and hence extensively used as an emulsifying agent. *Diethylene distearate* ($C_{17}H_{35}COOC_2H_4)_2O$ is also known as *glycostearin* (m. 54–55°C). The ordinary wax-like ester of propylene glycol, $CH_2OH \cdot CHOH \cdot CH_2$, is *propyleneglycol monostearate*. The commercial product melts at 48–49°C, or 10 degrees lower than the very pure synthetic ester.

One part of "*Diglycol Stearate S*" added to 10 to 30 parts of boiling water produces a stable milky emulsion. *Propyleneglycol monostearate* is a neutral, light-colored, waxlike solid which disperses readily in hot water. It is miscible with hot alcohols, hydrocarbons, and oils.

The preparation and uses of the polyhydric alcohol fatty acid esters have been publicized by the Glyco Products Company, manufacturers of these materials. *Diethyleneglycol monolaurate* is used in varnish to retard volatilization of the solvents, as a general plasticizer and softener, and in dyes for

carbon papers and typewriter ribbons; also in textile softening, leather finishing, and in cosmetics and polishes.

Suggested uses recorded for "*Diglycol Stearate S*" are the lubrication of spring leaves, the extrusion of aluminum tubing as a lubricant in making collapsible tubes, and as a treating agent for paper and cardboard to prevent breakage in stamping and embossing. It can be used as a suspending agent for pigments and abrasives, and hence is useful in making special cleaners, polishes and the like. It is used in conjunction with glycerol or alcohol for hand lotions and creams, which may be perfumed and colored if desired. When incorporated in salves and ointments it is said that stains from the unctuous material are washable. In alcoholic solution it may be sprayed on powders to prevent them from lumping. An ordinary grade of "Glycol Stearate S" is usable with glycerin in a temporary binder for abrasive powders that are to be later permanently fixed to abrasive and grinding wheels, or a temporary binder for clays prior to firing.

D-Sorbitol (1,2,3,4,5,6-hexane diol), $C_6H_{14}O_6 \cdot \frac{1}{2}H_2O$ (m. 89–93°C), forms both mono- and diesters with the fatty acids. The technical grades of *sorbitol stearates* melt within the range of 43 to 56°C.

Pentaerythritol (*2,2-bishydroxymethyl-1,3-propane diol*), $C(CH_2OH)_4$, (m. 255°C), forms several hydric esters with a fatty acid. *Pentaerythritol mono-*, *di-*, and *tetrastearates* are the better-known products. They range in melting point from 47 to 61°C, and are used as mold-release lubricants for molded plastic articles prepared from urea-formaldehyde plastic resins and the like. Certain modified fatty acid esters of pentaerythritol and its polymers are known commercially as "Pentowaxes." They can be readily mixed with other waxes, oils, and nonpolar solvents, and hence have proved of value in the preparation of polishes. The Heyden Chemical Company has discontinued the manufacture of "Pentowaxes."

Montan Glycolate Emulsifier

Breuer and Zentmyer Process. Breuer and Zentmyer[6a] have patented a process relating to the production of hard, gel-free waxes from montan wax which includes a partial esterification of free carboxyl groups by means of polyhydric alcohols.

In this process deresinified montan wax is treated with aqueous sulfuric acid solution of 47 per cent strength and the whole heated to 105°C. The stirring is begun just as soon as the wax becomes molten. The mixture forms a homogenous, emulsified mass within 15 minutes. Small additions of chromium trioxide dissolved in an equal amount of water are made in the course of 30 minutes. The temperature of the reaction mixture is maintained at 110–112°C. After the addition of the oxidant is complete, stirring

is continued for another 30 minutes at 110–112°C and boiling water is added to break the emulsion.

Heating is discontinued and upon standing and cooling a layer of wax separates from which the dark-green aqueous phase can be poured off. The wax is then washed with 47 per cent sulfuric acid and stirred vigorously at 95–100°C for 20 minutes. Upon cooling and separation of the wax, the wash acid is removed, and the wax is washed twice with water at a boil for 20 minutes each. After removal of wash water, the wax is dried by heating with stirring at 90–95°C and a pressure of 160 mm until foaming ceases, and the wax becomes clear and the temperature rises sharply. The cooled product is brown in color, and has a melting point of 79–84°C, and an acid number of 123. The yield is 62.8 per cent. A further bleaching treatment lightens the color and gives a product of 170 acid number, and 76–80°C melting point. The over-all yield is 54.2 per cent.

The bleached waxes are suitable for esterification with higher polyhydric alcohols containing 3 to 8 hydroxyl groups. For example, 100 parts of bleached montan wax may be esterified with 8.7 parts of ethylene glycol and 0.5 part of *p*-toluene sulfonic acid at 110–112°C in a stream of nitrogen gas. The esterified wax has an acid number of 34. The product may be further esterified with pentaerythritol to produce a wax with an acid number of 4.2, and melting point 75–80°C. After substantially all of the carboxylic acids have been esterified, minor portions of an unsaturated dicarboxylic acid or anhydride such as maleic anhydride may be added. After the mixture is heated for a number of hours the product is a light-brown wax with acid number of 9.28 and melting point of 73–80°C suited to use in the preparation of emulsion floor polishes.

Surface-Active Agents

The term "surface-active agents" is usually applied to water-soluble or dispersible materials that markedly *reduce* surface tension and interfacial tension. Through the use of these materials, it is possible to mix dissimilar materials such as oil and water, saving time and money by decreasing the natural reluctance of these materials to mix. It is also possible to disperse and suspend solids, such as wax, within a liquid. Surface-active agents performing this function are known as emulsifiers, dispersing agents, or solubilizers. They are widely used in the production of polishes, paints, textiles, cosmetics, pharmaceuticals, etc.

Chemically, surface-active agents are compounds in which one portion of each molecule is *hydrophilic*, or water-loving, and another portion is *lipophilic*, or oil-loving. The hydrophilic part of the molecule may, for example, be carboxylate, sulfate, sulfonate, polyhydric alcohol (see p. 534) or alcohol-ether. The lipophilic part of the molecule may be a long hydrocarbon chain,

as in the higher fatty acids, or a cyclic hydrocarbon, or a combination of the two. Surface-active agents may be classified as ionic or nonionic. The ionic types are either *anionic* or *cationic*. In soap, the anion (oleate, for example) is the effective portion of the molecule and soap is, therefore, classed as anionic. The petroleum sulfonates (see Emulsifying Agents, p. 530) are similarly classed as ionic.

In an ionic surface-active agent, the hydrophilic portion of the molecule is frequently weak. Its attraction to water may be increased by combination with an inorganic ion. Soap, for example, consists of an oil-soluble fatty acid chain with a polar carboxyl group whose water attraction is enhanced by neutralization with alkali. Because of its ionic character, it is sensitive to the presence of other ions. Thus, soaps are ineffective in hard water and electrolytes. The lipophilic characteristics of the surface-active agent greatly aid in the dispersion of waxes, and cationic surface-active agents such as triethanolamine stearate and ammonium acids soaps are frequently so used (see Emulsifying Agents, p. 530).

Nonionic surface-active agents depend chiefly upon hydroxyl and ether linkages to create the hydrophilic action. Since they do not ionize, they are comparatively insensitive to hard water and electrolytes. Typical of such nonionic surface-active agents are "*Tween*" and "*Span*" products (Atlas Powder Company).

The "Span"-type materials are essentially partial esters of the common fatty acids and hexitol anhydrides (hexitans and hexides) derived from sorbitol. The "Tween"-type materials are derived from "Span" products by adding polyethylene chains to the nonesterified hydroxyls, thereby increasing their hydrophile character.

Many of the "Spans" and "Tweens" are waxy solids and can be readily melted with waxes and resins prior to the addition of boiling water to disperse the ingredients. Those of particular interest in formulating wax polishes are "*Span 40*" (sorbitan monopalmitate), "*Span 62*" (sorbitan monostearate), "*Tween 40*" (polyoxyethylene sorbitan monopalmitate), "*Tween 65*" (polyoxyethylene sorbitan tristearate), "*Atlas G-9448-N*" (polyoxyethylene sorbitan monoöleate), and "*Atlas G-7426-N*" (polyoxyethylene sorbitan monopalmitate).

A dry-bright wax polish may be made from (a) *carnauba wax* 10, "*Atlas G-9446-N*" 3, and water 87 parts; (b) carnauba wax 5.0, *candelilla wax* 1.5, *paraffin* 1.0, congo gum (processed) 1.0, "Atlas G-9446-N" 3.0, and water 88.5 parts; (c) *carnauba wax* 5.0, *candelilla wax* 1.5, *paraffin* 1.0, congo gum 1.0, "Durez 219" 1.5, "Atlas G-9446-N" 3.0, and water 87 parts. In the preparation of the floor wax emulsions the waxes, resins, and emulsifiers are heated together at 100°C. Boiling water is added to the molten mixture with thorough agitation. Rapid cooling with moderate agitation promotes

fine particle size. The emulsions are bluish gray in color that have good resistance to water spotting, and are readily removed with hot water. The use of "Span" and "Tween" in furniture cleaner-polish not only brightens but protects the surface so treated.

"Abril" Waxes

"Abril Waxes" are ester waxes of a synthetic class produced in Great Britain by the Abril Corporation, Ltd., and in the United States sold by the Distributing & Trading Company, New York. The manufacturers have not disclosed the chemical composition of their waxes, but many of them are believed to be high molecular weight fatty acid esters of polyhydric alcohols.

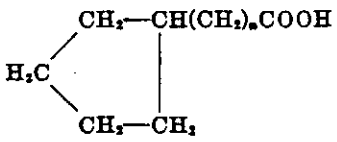
The full line of "Abril Waxes" include I, X, P, E, 8NS, 10DS, BJ, N, and ND. They range in acid values from 4 to 33, saponification numbers 90 to 200, and in unsaponifiable matter 9 to 32 per cent. All are soluble in hot organic solvents. The I, X, and E are hard waxes. The P wax is very hard. The 8NS and 10DS are medium-hard waxes. The BH, N, and ND are soft waxes. All of the waxes except 10DS and ND have a good compatibility with paraffin wax. In color they range from cream to brown except that 10DS is an odorless white wax. "Abril Wax X" melts at 68–74°C.

"Abril Emulsifying Waxes" are wax compounds which by the addition of alkalis or emulsifying agents or other suitable surface-active products, become of themselves powerful emulsifying agents. They are waxes which are capable of forming stable emulsions simply by the addition of water and/or solvents. Notably in the emulsifying wax class are "Abril Waxes" E (m. 78–82°C) and BJ (f.p. 58–62°C); and of the self-emulsifying types are N (f.p. 49–52°C) and ND (f.p. 66–70°C), both of which are dispersible in hot water.

"Abril Waxes" are used in the manufacture of shoe paste polishes, wax crayons, wax flowers, electrical insulation, cosmetics, packaging, cheese wrapping, textile waterproofing, printing inks, etc. "Abril X" of American manufacture finds an extensive use in paste polish and carbon paper manufacture.

Naphthenic Acids

Naphthenic acids are acid oxygenated compounds found in crude oils; basically they are monobasic carboxylic acids of the general formula R·COOH, where R is a naphthenic radical, a radical derived predominantly from cyclopentane or a homolog of cyclopentane. Naphthenes are saturated hydrocarbons containing one or more ring nuclei, and may have paraffinic side chains attached to the carbon rings. In the naphthenic acids of commerce the carboxyl group is most often attached to a side chain.



The best sources of naphthenes are the petroleum crudes of California, Venezuela, and Roumania. These crudes also contain naphthenic acids to the extent of 0.1 to 4.0 per cent. In the washing of top oils obtained in the distillation of such crudes these naphthenic acids may be recovered. When top oils are washed with sodium hydroxide, sodium naphthenates are formed, which when separated and treated with sulfuric acid form naphthenic acids and sodium sulfate. They are viscous liquids possessing a peculiar odor. The acids are then distilled (*in vacuo*) to purify them. When freshly distilled they are colorless and almost odorless.

Although naphthenates have little relation to waxes, they are of interest as one of the by-products in the preparation of paraffin waxes, and as substitutes for some of the liquid waxes used in the preparation of extreme pressure lubricants. Since they are good breakers of crude oil emulsions, they are used as an ingredient of a number of proprietary oil-emulsion breakers. They possess excellent solvent properties towards rubber, resins, and tars. Naphthenic acids are fused with metallic oxides for the purpose of producing dryers for paints, enamels, etc. Naphthenates of manganese, cobalt, and zinc are used as driers in paints and lithographic inks. Lead naphthenate is used in extreme pressure lubricants where it is desired to impart a rupture strength of 8000 pounds or more to the sperm or rape oil film. Sodium naphthenate shows a low degree of hydrolysis and hence is highly valued as a scouring agent in textile mills, particularly in scouring and felting of wool. Calcium naphthenate is used in motor oils as a detergent. Copper naphthenate is used in mildewproofing fabric for sand bags. The United States produces about 30 million pounds of naphthenates per year, and imports about 12 million pounds from Netherlands West Indies. Lead naphthenate accounts for almost half of the total production, followed by lesser amounts of the naphthenates of cobalt, manganese, calcium, and zinc.

"Napalm" used by the Armed Forces is an aluminum soap prepared from an oleic, naphthenic, and coconut oil acid mixture[45].

WAX EMULSIONS FOR SPECIFIC USES

Antifreezing Wax Emulsions

It is a common practice to employ material in automobile radiators to prevent the freezing of the water at low temperatures. Some of the more desirable antifreeze agents are glycerol, ethylene glycol, diethylene glycol,

and other polyols. These agents have a tendency to foam in use, and Flaxman[14] has proposed an antifoaming wax-base composition as an additive to the antifreeze agent of the polyol type. *Montan wax* which has been partially saponified is dissolved in lard oil or mineral oil to the extent of 1 to 5 per cent. The antifoaming agent may be prepared from water 20, montan wax 4, potassium hydroxide (dry) 0.25, and glycerin 25 parts. The wax is added to most of the water; the KOH in solution in the rest of the water is slowly added. The mixture is brought to boiling. After 20 to 30 minutes of boiling the glycerin is stirred in and the mass agitated at about 93°C (200°F) for 10 minutes and then cooled. The boiling brings the glycerin content to about 60 per cent. There must be no excess of KOH after saponification. The cooled mixture is then admixed with 50 parts of lard oil, castor oil, or mineral oil of appropriate consistency.

A good formula for a concentrated antifreeze solution containing the foam-preventing agent would be the following: water 20, glycerin 79, lard oil 0.5, antifoam agent, as first described, 0.5 parts. The water is charged into a kettle and about 10 per cent of glycerin mixed therein. About 25 per cent of the antifoam agent is stirred in, and the remainder of agent and lard oil are then added slowly with rapid agitation. About 0.1 per cent of sodium silicate is added and the antifreeze product packaged for use.

Emulsions for Finishing Fibers

In the textile industry the emulsion may be prepared at the point of use with suitable emulsification equipment. The composition consists of more than 93 per cent of oil or wax and the remainder a cationic emulsifier, which need not necessarily be soluble in the wax. If required, the concentrated form of the emulsion is homogenized. The emulsion is then diluted with sufficient water to provide proper weight application to the given amount of textile (e.g., wool). Owing to the cationic nature of the emulsifier, the emulsion particles will be charged, and they will discharge onto the wool fiber and the oil or wax will be deposited directly onto the wool.

Waxes that cannot be classified as emulsifiable can nevertheless be emulsified by dispersing (suspending) them in highly emulsifiable ionic agents. For example, 10 parts of ammonium linoleate are added to 500 of water; to this mixture 50 parts of melted *carnauba wax* are added. Such an emulsion has been suggested by Muller[31] for finishing furs, such as lambskins, etc. The furs to be treated are immersed in a solution comprising carnauba wax emulsion 20, aluminum formate 20, phthalic acid 20, ethyl lactate 10, formaldehyde 30, and water 900 parts. They are then hydroextracted, roughly dried at 100–120°F, flashed at 240–250°F, brushed, and ironed.

Crude scale wax can be emulsified with stearic acid and ammonia water at 123–125°F to produce an anionic emulsifier, suitable for surface-treating

hemp or other vegetable fibers which are fabricated into rope to make the fibers resistant to wear and the detrimental effects of water. *Refined woolwax* and commercial *beeswax* are emulsified directly with ammonia water, as: wax 10, strong ammonia water (26°Bé) 3, and water 87 parts. Crude scale wax emulsions are preferred because of their cheapness.

Suitable wax finishes are marketed for laundered fabrics such as women's wear, curtains, sleeping bags, uniforms, sports clothes, rainware, children's clothes, etc.

Wax Finishes for Metal

Rust-inhibiting wax emulsions are made in clear and black colors for finishing hardware, padlocks, stovepipe, kitchen utensils, garden tools, bolts, screws, typewriter and camera parts, etc. They are of the W/O type. The finish protects metal surfaces against corrosion, provides a dry lubrication, and adds to the appearance and beauty of the object coated. Wax finishes are also produced to enhance the beauty of plastic objects.

Wax Finishes for Rubber Goods

Wax finishes give a gloss to such rubber pieces as rubber tile, rubber heels, rubber-covered wire, toilet ware, industrial hose, toys, gaskets, battery boxes and stair treads. The finishes can be applied by spraying, dipping, wiping, or roller coating, depending upon the shape of the piece to be coated.

WAXY ALCOHOLS

When fatty alcohols were first marketed in commercial quantities more than a score of years ago, they were derived from sources which contained them either free or in the state of combination, such as spermaceti or sperm oil, by a process of splitting the fatty acid and unsaponifiable by saponification, and recovering the alcohols from the unsaponifiable matter by further refinement. The fatty alcohols per se are primary alcohols which have an even number of carbon atoms in a straight chain from C_8 to C_{20}. The commercial fatty alcohols include octyl (C_8), decyl (C_{1}:), lauryl (C_{12}), myristyl (C_{14}), cetyl (C_{16}), stearyl (C_{18}), and oleyl (unsaturated, C_{18}). Of this group only saturated alcohols C_{16} (m. 49°C) and C_{18} (m. 58.5°C) can be designated as *waxy alcohols.*

Today, fatty alcohols are made from fatty acids by several processes, the predominating ones being the *sodium-reduction* process and the *hydrogenolysis* process. In the "Bouveault-Blanc process"—originated in 1903 but not commercialized until thirty years later—the reduction of the fatty acid is effected by the use of metallic sodium. It utilizes hydrogenated tallow as the source of raw material. All operations are conducted at at-

mospheric pressure in conventional mild-steel reactors. A solution of ester, reducing alcohol (i.e., methylisobutyl carbinol), and solvent (e.g., toluene) is fed into a reactor containing metallic sodium suspended in a solvent inert to sodium. An exothermic reaction occurs yielding a solution of sodium alcoholates, which is then fed into a reactor containing water, resulting in hydrolysis of the alcoholates and the formation of a two-phase system—an organic layer consisting of solvent, reducing alcohol, and fatty alcohol and an aqueous caustic layer which contains glycerol and water-soluble alcohol, if any. The caustic layer is separated and the fatty alcohol is recovered from the organic layer by removing the solvent and the reducing alcohol (methylisobutyl carbinol).

The hydrogenolysis process, as exemplified by the De-Nora process, originated in the 1930's. Fatty alcohols are produced by the catalytic hydrogenation of fatty acids split from tallow, employing copper chromite as catalyst, under conditions of high pressure and high heat. The pressure range is from 100 to 300 atmospheres and the temperature range from 200 to 350°C. The upper limits of pressure and temperature are likely to lead to the formation of hydrocarbons through overhydrogenation. In the De-Nora process the fatty-acid feed stock should contain less than 6 per cent of oleic acid. The feed is preheated to 304°C and fed, together with powdered catalyst and preheated hydrogen, to the bottom of an electrically heated high-pressure reaction chamber. The reaction takes place at 335–338°C and 3500 psi. When the hydrogen absorption has slowed, the batch is discharged and filtered to remove the catalyst. The alcohols are purified by distillation. Since the raw material—tallow—is less costly than hydrogenated tallow, and sodium is not required, the hydrogenolysis process is more economical than the sodium reduction process, although this difference is largely offset by the higher cost of hydrogen and catalyst in the sodium-reduction process.

Saturated fatty acids are reduced to the alcohols in the presence of 10–30 per cent of cupric stearate with hydrogen at a temperature of 250–300°C, and pressure of 2000–3000 psi in 2–12 hours time. For example, 30 g *cupric palmitate* in 120 g of palmitic acid was heated in a rocking autoclave 4 hours at 275°C with initial and final pressures of 2300 and 2070 psi, which according to Kunz and Fiore gave a product when filtered that contained 97.5 per cent of acetylizable constituents as cetyl alcohol with no hydrocarbon formation. [Kunz, E. C., and Fiore, A. J., U. S. Patent 7,590,105 (1952).]

The present annual production of fatty alcohols (by sodium-reduction and hydrogenolysis processes) is estimated by Wilson[47] at 130 million pounds, the sodium-reduction route accounting for nearly 80 per cent of this total.

In the "Oxo" process, olefins react with carbon monoxide and hydrogen

under high pressure and temperature to yield aldehydes with one more carbon atom than the starting olefin. Hydrogenation of the resulting aldehydes yields a mixture of primary alcohol isomers. If the olefin has an even number of carbons the synthesized products contain a certain percentage of normal primary alcohols having an uneven number of carbon atoms mixed with side chain alcohols. In this respect the alcohol product differs from the fatty alcohols produced from natural sources of material. The Oxo process was first more or less confined to producing primary alcohol isomers of C_5 chain length; it is now being adapted for producing alcohols of C_{10} and C_{13} chain length, namely primary decyl and tridecyl alcohols.[37]

In the "Leader process"[26a] wax is the source of raw material. The wax is saponified with an excess of alkali, and propane, ethylene, butene, propylene, or a mixture of one or more solvents is added in the proportion of 3:1–10:1 in a mixing zone at 100–150°F, and 225–300 psi. The mixture is settled to remove the soap stock, and the alcohol is either recovered immediately by stripping off the solvent or diluted with a further addition of solvent to a ratio of 10:1–40:1, and fractionated at 160–205°F and 450–700 psi with a saturated top fraction and an unsaturated bottom fraction while a temperature gradient of 3–8°F is maintained in the column. The process is applicable to beeswax, candelilla wax, montan wax, crude sperm oil, spermaceti, etc.

Cetyl Alcohol and Derivatives

Cetyl alcohol, $C_{16}H_{33}OH$, is a waxy material for which there is a fairly large commercial demand. It was discovered by Chevruel in 1813, who isolated it by the saponification of spermaceti, extracting it from the aqueous soap solution by means of petrolic ether. To secure a good yield it is best, according to Axelrad[3], to prepare it from the calcium soap of spermaceti; this method is said to yield 40 to 45 per cent of cetyl alcohol. In this process, 15 parts of melted spermaceti are mixed with 20 parts of lime containing 5 per cent of water, heated and stirred for six hours, the water being distilled at 100°C. Then the temperature is allowed to rise to 340°C when the cetyl alcohol distils off in the form of oily drops which solidify to a white mass (m. 49.5°C) on cooling. The distillation can also be conducted *in vacuo* at a lower temperature, thus yielding an improved product. Cetyl alcohol can be similarly prepared from hydrogenated sperm oil, or by directly hydrogenating spermaceti or sperm oil with a catalyst in a pressure reaction vessel using high temperature and pressure (see p. 275).

Cetyl alcohol is produced in the form of white crystal; specific gravity (d_4^{15}) 0.811 at 15°C, and ($d_{15}^{49.5}$) 0.8176 at its melting point; melting point 47–49°C; boiling point 344°C; refractive index (n_D^{79}) 1.4283–1.4288. It is insoluble in water; soluble in alcohol, chloroform, ether. Cetyl alcohol is

produced in both technical and NF grades. Mlle. Delcourt[8] prepared a very pure cetyl alcohol and determined its physical constants as melting point 49.10°C; specific gravity (d_4^{55}) 0.81521, (d_4^{75}) 0.80157, (d_4^{100}) 0.78395; and viscosity (η^{60}) 0.134, (η^{60}) 0.0842, (η^{75}) 0.538 CGS units.

Cetyl alcohol is used in the manufacture of the sulfated alcohol for textile soap; as an emulsifier, and in metal drilling lubricants (see p. 275). The NF grade is used in medicine, perfumery, emulsifiers, and cosmetics; it is of value for chapped skin and eczema. A use in cosmetics is as a substitute for lanolin; e.g., when 10 parts of *cetyl alcohol* are used in conjunction with *petrolatum* 70, *paraffine* (m. 60°C) 20, and *anhydrous lanolin* 5 parts, and the mixture is ground with 100 parts water, a good substitute for lanolin for many purposes is obtained.

Cetyl Esters

Cetyl esters, consisting largely of *cetyl palmitate*, can be produced from *sperm oil* by light hydrogenation. The product is marketed under the name of "Cetiol." When sperm oil is thus hydrogenated the triglycerides (including glyceryl ethers) which are undesirable are separated by mild saponification in the cold. The cetyl esters product is a diaphanous, crystalline, odorless and tasteless mass closely resembling spermaceti and contains 75–85% of compound *cetyl esters*, 2–4% of *triglycerides*, and 10–20% of *cetyl alcohol*[35]. It is of value in the production of certain types of cosmetics, e.g., lipstick. "Cetiol" is suitable for uses where it is desired to have a liquid fatty wax of good penetrating power; e.g., it is used to replace mineral oil in a superior nonfoaming type of shampoo.

One of the newer commercial cetyl alcohol derivatives is *dicetyl ether*. This is a soft, waxy, nontoxic material; it has been suggested as a plasticizer, water-repellent impregnating agent and oil additive, plastic molding lubricant, dielectric, perfume fixative, and cosmetic constituent.

Fatty alcohols (of 8–20 C atoms) may be obtained, according to Steinberger[38], by saponifying related fatty acid esters in the presence of water-miscible solvents (b. 200–350°C) and distilling the mixture from which the alcohol is separated by controlled dilution with water; the solvent may be recovered by distillation of the aqueous solution. For example, spermaceti may be saponified in the presence of triethylene glycol, and cetyl alcohol recovered in the aforesaid manner.

Stearyl Alcohol

Stearyl alcohol (1-octadecanol, *n*-octadecyl alcohol), $CH_3(CH_2)_{16}CH_2OH$, formula weight 270.49, is a waxlike substance. It melts at 58.5°C, boils at 210.5°C at 15 mm pressure, and when melted has a density (d_4^{59}) of 0.8124. Its natural source is the sperm and blubber oil of the whale, porpoise, and

dolphin. Stearyl alcohol of commerce is prepared by the reduction of sperm oil and hydrogenated cottonseed, corn, and sunflower oils. There are also several methods by which stearyl alcohol can be synthesized.

Stearyl Alcohol USP is defined as a mixture of solid alcohols consisting chiefly of *n*-octadecyl alcohol. It occurs as unctuous white flakes or granules, and has a faint characteristic odor and a bland, mild taste. It is insoluble in water but soluble in alcohol and in ether. It melts between 56° and 60°C. The USP limits the acid and iodine value to 2 maximum, and the hydroxyl value to not less than 200 nor more than 220. The method of determining the hydroxyl value is fully detailed.

Stearyl alcohol, like cetyl alcohol, is used as an ingredient in ointment bases, cosmetic creams, lotions, etc. Official preparations that include stearyl alcohol are hydrophylic ointment and hydrophylic petrolatum (USP XIV) and NF sun cream (NF IX). It is also used as an emulsifier, finishing agent, antifoam agent, and lubricant additive, and in rubber processing. Phosphated stearyl alcohol is used as a suppository base. The esters of stearyl alcohol with organic acids have many and varied medicinal and industrial uses[12].

WAXY ACIDS

Aliphatic Waxy Acids

Many of the higher molecular weight acids of the fatty acid series, $C_nH_{2n}O_2$, are of waxy consistency. Those better known commercially are lauric, myristic, palmitic, stearic, arachidic, and behenic acids. Although the acids of still higher carbon content are even more waxy, they are not easily obtainable for industrial use. Hydrogenated tallow fatty acids contain 3 per cent of *myristic*, 28–29 per cent *palmitic*, 63–66 per cent *stearic*, and 6–2 per cent of *oleic acid*. Hydrogenated fish fatty acids contain 4–8 per cent of *myristic*, 32–29 per cent *palmitic*, 22–18 per cent *stearic*, 23–26 per cent *arachidic*, 13–17 per cent *behenic*, and 6–2 per cent *oleic acid*.

During World War II the United States industry used almost 500 million pounds of *waxy* fatty acids a year, and their consumption has been increasing steadily. Their use dates back to Chevreul who in 1815 discovered that tallow could be treated chemically to yield glycerol and hard, high-melting, *waxy* fatty acid, and that candles made from these fatty acids can be burned without giving off an irritating gas.

Preparation of Waxy Acids

There are six methods of splitting ordinary vegetable oils and animal tallows into glycerol and fatty acids. These are (1), the Twitchell process which is one of acid hydrolysis assisted by a catalytic agent; (2), the Autoclave process, pioneered by Tilgman and Berthelot in France in 1854, which

is one of hydrolysis of the fat or vegetable oil by water; (3), the Alkali Saponification method; (4), the Continuous processes, essentially improved hydrolysis-by-water methods; (5), the Enzyme Hydrolysis method of fat-splitting; and (6), the Emersol process of selective-solvent crystallization of fatty acids obtained by fat-splitting under great pressure followed by distillation.

(1) In the *Twitchell process*, developed by Ernst Twitchell, in 1898, the triglyceride oils and fats are boiled with live steam in open tubs with dilute sulfuric acid and a chemical catalyst (such as naphthalenestearosulfonic acid) for from 18 to 20 hours or more. This causes the water to react with the fats, liberating fatty acids and glycerol. The fatty acids are then separated by running off the "sweet water" containing the glycerol. The fatty acids after a second acid boil must then be separated by fractional solvent crystallization or by vacuum distillation, to free the waxy from the liquid fatty acids (red oil). (Also see p. 551.)

(2) In the *Autoclave process* 20,000 to 30,000-pound batches of oil or fat are heated in closed vessels with water at a steam pressure of 150 to 250 pounds per square inch for from 4 to 10 hours. No catalyst is used in the process. The fatty acids when separated from the water-soluble glycerol are refined to obtain the waxy fatty acids of commerce.

(3) In the *Alkali Saponification* method the triglycerides are treated with strong sodium hydroxide in large open kettles. Under the influence of open steam heat and agitation this treatment converts the fats into soaps and glycerol. The soap is salted out, and washed with salt water to remove impurities, after the glycerol and spent lye have been withdrawn from the bottom of the kettle. Sulfuric acid is added to the soap to set free the fatty acids, which upon withdrawal are fractionated to obtain the more waxy acids.

(4) In the *Continuous process*, developed by Martin H. Ittner[24] in 1938, the fat is dissolved in water in a pressure reactor, designed to keep the water in a liquid stage at a very high temperature. For example, as much as 23 per cent of the fat is known to dissolve in water at 245°C (473°F). A finely divided stream of oil is allowed to rise through a tall column against a downward flowing current of water at relatively high temperature and pressure. As the droplets of oil trickle upward through the hot water they partially dissolve and react with the water to form glycerol and fatty acids. The glycerol is carried away by the downward moving column of water as fast as it is formed. By the time the oil droplets reach the top of the tower, the fat has been entirely converted to fatty acid (also see Continuous Processes for Splitting Fats, p. 306d).

(5) The *Enzyme Hydrolysis* method of fat-splitting is more suitable to vegetable oils and tallows than to animal fats. Enzymes of plants, such as

the *lipases* in seed whose biological function is to render the fat of the seed available during the germination process, have also fat hydrolyzing properties in the presence of weak acids. An active form of lipase is that of the castor bean which functions well with oils at a pH of 4.7–4.8, particularly so in a water-in-oil emulsion at a temperature of about 35°C. The hydrolysis of vegetable oils or tallows is conducted by mixing about 3–8 per cent of a suitably prepared lipase with fat containing 40–50 per cent of water, adding a little acetic acid and manganous sulfate as an activator, and permitting the mixture to stand at 35°C for one to two days, with frequent stirring. In this hydrolysis the fatty acids separate to the top with more or less hydrolyzed fat. The middle layer which is an emulsion of fat and albuminous material is somewhat difficult to separate, but when recovered has value for soapmaking. The lower layer contains the glycerol. Light-colored acids are obtainable by this method but not with an entirely satisfactory yield. There exist numerous other hydrolyzing enzymes, some of which are very effective with esters of low molecular weight, and are known as *esterases*.

(6) Emery Industries, Inc., employs the Colgate-Emery process for the continuous distillation in corrosion-resistant equipment at a high vacuum. Automatic controls throughout provide a uniformly pure, high quality fatty acid product, which can be freed from oleic acid by the Emersol process of selective-solvent crystallization at a controlled temperature. A polar solvent such as methyl alcohol of 90 per cent strength is employed. The process makes obsolete the pressing methods which are more costly and uncertain as to the quality of the finished product. Metal contamination, ash content, and mineral residues are eliminated, factors of importance in the candle, cosmetic, and other industries[2]. See Continuous Process of Solvent Crystallization, p. 553.

Continuous High-Temperature Fat-Splitting Processes

Continuous high-temperature processes for the splitting of fats are in favor by the larger corporations. Of the continuous processes one is *concurrent* (Eisenlohr)[10] and the other is *countercurrent*. The countercurrent continuous process is found in two modifications; one is known as the Proctor and Gamble process (Mills)[10], and the other is the Colgate-Emery process (Ittner)[23e], which is employed by Armour and Company at a plant at McCook, Illinois, designed for processing 100,000,000 pounds of raw fats and oils per year[10].

Fats received by the plant are refined and hydrogenated, except the vegetable oils. Refining is done by means of dilute alkali and bleaching. The filtered fat or oil is hydrogenated in stainless steel (type 316) clad vessels, of which there are five having a charge capacity of 10,000 pounds each. Raw

hydrogen containing CO and CO_2 is prepared by catalytic reaction of natural gas and steam in a standard plant unit. The hydrogenation is carried out at 150 pounds per square inch (psi) pressure and 175–200°C temperature, using about 0.25 per cent by weight of the catalyst (nickel formate). After completion the charge is blown to stainless steel filter presses. Nitrogen pressure forces the oil through filter paper, removing the catalyst. The filtered oil is pumped to a large tank where it awaits transfer to the splitter for the preparation of the fatty acids.

In the Colgate-Emery process for high-temperature splitting, the principle of which has been previously described under method 4 (Ittner method), the countercurrent reaction is conducted in a pressure tower with internal exchange. A light-colored fatty acid is obtained with a splitting efficiency of about 98 per cent. A good grade of fatty acid can be obtained from good stock without resort to distillation. Pressures of about 650 psi and temperatures of about 245°C are employed. Temperatures, pressures, and flow rates are regulated by pneumatic controllers. The column is a 3 × 67 foot shell unit lined with stainless steel (type 316) spot-welded to the tower shell which is heavily insulated with magnesia block. Both fats and water are charged into the column by means of three vertical triplex pumps. Fat is charged into the column through a sparge ring which breaks it into small droplets, and rises through the hot "sweet water" into the fat phase where it is heated by direct contact with steam sparged into the lower sector of the column at about 245°C. Hydrolysis of the glycerides takes place as the material continues to pass upwards. The sweet water contains 10–12 per cent glycerol, which is recovered.

Fractional Distillation of Fatty Acids

The fatty acids from the splitter pass directly to the crude fatty acid storage tank to await distillation. In the distillation plant at Armour & Company a triple-column system is used. All three stills are bubble-plate units of stainless steel (type 316), designed for a very low pressure drop. Each is fitted with a shell-and-tube condenser which is connected through a catch pot, to a barometric condenser and to a two-stage steam-jet ejector. Each still has a "Dowtherm" reboiler near its base. The system has a capacity of handling 3500 pounds of fatty acids feed per hour. The stills are operated at constant pressures and a maximum base temperature of 250°C. An "odor cut" is first taken off at 40 mm pressure, but the higher fatty acids are taken off at 5 mm pressure. The "bottoms" from the still go to the stearine pitch tank. In the distillation plant the feed stock is refined vegetable oil, hydrogenated animal tallow, or marine tallow-fatty acids, depending upon the particular fatty acid or acids desired.

The final step in the preparation of the high melting acids is to pump the

molten acid to a smaller steam-heated tank from which the liquid is pumped to *rotary drum flakers*. The molten stream is fed at constant rate through a trough from which the overflow returns to the feed tank. A chromium plated rotating drum chilled by an internal spray of water dips into the trough, picking up a thin film of the acid which solidifies. After a 270-degree turn, the solid film is removed by a scraper, falls into a conveyor hopper, and is carried to a bag filter which collects it into 50-pound paper bags.

Distillation of Fatty Acids by Batch Process

In a typical Garrigue distillation plant used for distilling commercial fatty acids produced by the batch process, the still is charged with 15,000 pounds of fatty acids and the temperature raised to 232°C (450°F). The rate of distillation is gradually increased by the introduction of superheated steam until 1500–2000 pounds per hour are distilled. The temperature of the cooling water when the still is operating at optimum capacity is maintained at 32–38°C (90–100°F). The still and superheater furnaces must be fired uniformly in order to maintain uniform temperatures and distillation. The yield of *double-distilled fatty acids* from cottonseed foots is about 85 per cent, and 12 per cent pitch. Rotary vacuum pumps are used for pulling dry vacuum off a countercurrent barometeric condenser. "Mixed fatty acids" as marketed may consist of double-distilled cottonseed, corn, animal, linseed, soybean, or hydrogenated fish oils. The pure fatty acids are marketed in various types of purity depending upon the source of the feed stock.

Murumurú seed fat, a vegetable tallow obtained from the kernels of the fruit of the palm, *Astrocaryum murumurú*, indigenous to Brazil, is the source of *lauric* and *myristic acids*. The kernels yield 36 to 42 per cent of tallow which contains *lauric* 40, *myristic* 34.5, *palmitic* 4, and *oleic acid* 10 per cent. Murumurú seed fat is also known as Murumurú palm kernel oil. Palm oil provides the best source of *palmitic acid* (42.5 per cent). Beef tallow provides the best source of *stearic acid* (18.5 per cent). The range of commercial acids is between C_{12} and C_{22}, but the C_{14}, C_{16}, and C_{18} acids are the more important.

The Armour Chemical Division produces *caprylic*, *capric*, *lauric*, and *myristic acids* of high purity, which they designate as "Neo-Fat" 8, 10, 12, and 14 respectively. They are prepared from ordinary distilled coconut oil fatty acids, by further fractional distillation. In this manner they are able to market C_8, C_{10}, C_{12}, and C_{14} acids, having an iodine number of 1.0 maximum, accompanied by high acid values and higher titers than those of similar acids produced from other raw materials.

White alkyd resin enamels, owing to the presence of unsaturated fatty acids in the raw material, have a tendency to yellow on aging. When a

high-purity lauric acid containing less than 1 per cent of unsaturated acids is used to formulate a high-bake alkyd resin enamel, it will provide a finish which is permanently tough and flexible, and which will stay white.

Distillation of Fatty Acids by Continuous Process

Improved results in simple distillation of fatty acids are obtained by continuous operation under high vacuum and relatively low temperature with indirect heating by "Dowtherm" vapors. Prior to simple distillation the feed stock is deaerated before heating and the crude fatty acids vacuum dried at low temperatures. The maximum operating temperature when distilling a mixture of fatty acids with a vapor pressure of 5 mm Hg at 400°F, actually would be about 400°F. This is a considerable improvement over the direct fired pot type stills in which distillation temperatures reach 500° to 550°F. For 1000 pounds of distilled fatty acids the improved continuous process uses 3½ gallons fuel oil in contrast to 15 gallons required for conventional pot stills.

Continuous Process of Solvent Crystallization

In the solvent crystallization of higher fatty acids, a continuous process of fractional crystallization using a solvent such as methanol (90 per cent) has put this separation on an economical basis for large-scale production. In the typical unit of this type, refrigerated cylindrical vessels with internal scraper blades reduce the fatty acid solvent mixture to a slurry, which is then filtered on a drum-type vacuum filter. The solvent is then distilled from the two-separated fractions. In addition to solvent crystallization, various methods of liquid-liquid separation are being employed, depending upon the differences in solubility of various saturated and unsaturated acids in solvent at different temperature levels. Liquid propane has a preferential solubility for saturated acids; and furfural for the unsaturated, lower molecular weight materials.

Acids from Paraffin Wax

The fatty acids that have been so far directly obtainable from the paraffin waxes are limited to those of lower molecular weight, and comprise those with an odd number of carbon atoms not ordinarily found in fats. For example, Fischer and Schneider[13] heated paraffin and dilute sodium hydroxide at 170°C with air under pressure and a catalyst (Fe, Mn, and Cu); they obtained a 95 per cent yield of *nonadecanoic* ($C_{19}H_{38}O_2$, m. 65–66°C); *heptadecanoic* ($C_{17}H_{34}O_2$, m. 58–59°C); *pentadecanoic* ($C_{15}H_{30}O_2$ m. 50–51°C); and *tridecanoic* ($C_{13}H_{26}O_2$, m. 38°C) acids. Paraffines containing not only aliphatic hydrocarbons, but cyclohydrocarbons as well, do produce complexities.

In the process of converting paraffin wax to the fatty acids the wax mass mixed with a suitable catalyst is subjected to large amounts of air at a prescribed temperature and pressure. After temperature, catalyst, and time, the quantity of air used in relation to the unit mass of paraffins has been recognized as the most important variable, according to Pardun and Kuchinka[33]. Grün and Ulbrich[18] in 1923 oxidized a paraffin for 12 hours at 160°C using 150 to 1200 liters of air an hour, and concluded that 500 liters of air was the optimum. Pardun and Kuchinka oxidized a paraffin produced in the Fischer-Tropsch synthesis. The wax had a solidifying point of 37°C, and a saponification gravity of 0.779. The glass apparatus served for oxidizing 50-gram samples and the allowance of air varied from 50 to 2½ liters an hour. The oxidation rate rose toward an optimum as the quantity of air used increased and then leveled off during the whole temperature range in intervals from 100° to 160°C. If excessive air flowed through, considerable material was blown out.

Ellis[11] states that in the oxidation of paraffine the waxes used melt at 52 to 57°C (the temperatures between 150 and 180°C), and that the application of increased pressure speeds up the reaction when air is used as the oxidizing agent. By withdrawing the partially oxidized wax and adding fresh wax to the reaction zone the darkening of the resultant fatty acids may be avoided. Wax acids produced with a 52°C melting point wax consist of both fatty and hydroxy acids as well as their anhydrides, lactones, and lactides. The hydroxy acids correspond to the formula $C_{13\text{-}17}H_{25\text{-}34}OH$—COOH. Catalysts of manganese, nickel, chromium, and cobalt result in a higher yield of acids.

Calcium naphthenate has been found to be a good catalyst for the oxidation of petrolatum, under certain conditions of temperature and pressure. Oxidations of paraffin with a naphthenate catalyst can be conducted at 120–140°C. The reactions can be restrained so as to produce considerable amounts of aldehydes and alcohols rather than acids, as by a patented process using orthoboric acid. A mixture of the crude alcohols had a melting point of 34°C. When refined the alcohols had a density of 0.860 to 50°C, a melting point of 31.5°C, and a low acid number, 0.9. There are quite a number of processes for the industrial production of the so-called wax acids, such as passing the molten paraffin and air concurrently through a multiple-section heated tower[15].

It has been reported that in Germany fatty acids have been successfully obtained from the paraffin waxes of brown coal. The process employs oxygen-enriched air in the presence of a metal catalyst, with suitable temperatures and pressures. The end products from a representative run are *capric*, *pelargonic*, *lauric*, *hendecanoic*, and other acids containing from 10 to 18 carbon atoms, or of even greater molecular weight. For practical purposes, the

acid mixture is saponified and unsaponifiable residues are returned to the reaction process. To be commercially profitable a highly efficient plant and management are required. It is also reported that when these fatty acids are esterified with synthetic alcohol they have been used as edible fats.

The uses of synthetic fatty acids prepared from paraffin waxes are many. The largest use appears to be in the manufacture of soaps. In insecticide sprays containing kerosene the wax acids are superior to green soap. They are also extensively used in the treatment of lubricating oils.

Acids from Oils and Fats

Fatty acids are marketed as "mixed fatty acids" and "pure fatty acids," or under other suitable designation. The mixed fatty acids may consist of double distilled cottonseed, corn, animal, linseed, soybean, or hydrogenated fish oils. The pure fatty acids are marketed in various types of purity depending upon the source of the raw material and the method of preparation employed. The range of commercial waxy acids is between C_{12} and C_{22} the C_{14}, C_{16}, and C_{18} acids being by far the more important.

The solubilities of the pure fatty acids in organic solvents rapidly decrease with a rise in the molecular weight of the acid. For example, the solubility at 20°C of *lauric acid* in grams per 100 ml of 95 per cent ethanol is 72.8, of *myristic acid* 15.1, of *palmitic acid* 3.9, and of *stearic acid* 0.9. The solubility of lauric acid in chloroform at 20°C is 124, of myristic 48.4, of palmitic 22.5, and stearic 3.8[1].

The waxy nature of these fatty acids and of their derivatives such as amines, nitriles, ketones, and amides, causes them to play an important role in wax technology. The field thus far has been largely in soaps, candles, cosmetics, shaving creams, buffing compounds, soaps, and mechanical rubber goods, but it is being rapidly extended.

Fractionally Distilled Fatty Acids

The new technique of fractional distillation of fatty acids, according to Stingley[39], has opened up an entirely new field of aliphatic chemistry as the pure acids produced furnish a means of making a myriad of derivatives for application in every field of chemistry. Stingley has tabulated the characteristics of the new commercial fatty acids (C_8–C_{18} range) in comparison with the chemically pure fatty acids. If in addition to the distillation a hydrogenation procedure is utilized, such as that of certain saponified fish oils, *arachidic* (C_{20}) and *behenic* (C_{22}) *acids*, which rarely occur in nature, can be produced. Lewkowitsch in 1907 was the first to apply the Sabatier and Sendesens synthesis in reducing the oleic acid quantitatively to stearic acid by means of hydrogen in the presence of finely divided metals.

Armour and Company offer a vacuum-distilled c.p. stearic acid under

the designation "Neo-Fat No. 165." This stearic acid has a melting point of about 67°C (152.6°F). It contains 90 per cent *stearic*, 6 per cent *palmitic*, and 4 per cent of *oleic acid*. It has an iodine number of 3.0 (Wijs), and an unsaponifiable content of 0.5 per cent. A specimen examined by the author had a melting point of 66.7°C (152°F); softening point of 66.7°C; durometer hardness of 68 at 34°F, 75 at 75°F; and a specific gravity (d_{15}^{25}) 0.0988, and (d_{15}^{5}) 0.9145.

Stearic Acid

Stearic acid is a whitish crystalline solid in the pure state, and is the C_{18} member of the series of saturated fatty acids having the structural formula

$$R{-}\overset{\overset{O}{\|}}{C}{-}OH$$

where R is $CH_3 \cdot (CH_2)_{16}$. Though not a wax, stearic acid is so widely used as a wax in candles, cosmetics, crayons, etc., that it is deserving of being grouped with the waxes. *Commercial stearic acids* contain 6–51 per cent of the C_{16} member of the series, namely *palmitic acid*, and 1 to several per cent or more of *oleic acid*, depending upon the grade. USP stearic acid, while containing a large proportion of palmitic acid, contains less than 1 per cent of oleic acid. Stearic acid in its crude state is often referred to as "stearine."

The name "stearine" is now and then confused with "stearin." Publications are sometimes negligent in retaining the final "e" on the word stearine when they refer to commercial stearic acid. *Stearin* is the fat known chemically as *glyceryl tristearate*. Stearin in nature is always accompanied by other glycerides of fatty acids, such as *olein* and *palmitin*. It is for this reason that commercial stearic acid which is dependent upon glycerides as the source of raw material does contain fatty acids other than stearic. Stearin derives its name from the Greek word for tallow.

Stearic acid is prepared by the saponification of stearin, e.g., the stearin may be saponified by alkali and the stearic acid set free from the alkaline stearate by means of a mineral acid, but the shorter and more economical method is to hydrolyse (split) tallows or greases by steam or acid as in the processes described later, and then sweat out the stearic acid from the mixed fatty acids by filter-pressings, or to recover the stearic acid by certain newer processes which make filter-pressing unnecessary. The splitting of glycerides yields not only fatty acid but glycerol as well.

$$\underset{\textit{stearin}}{C_3H_5(O \cdot CO \cdot C_{17}H_{35})_3} + 3HOH \rightarrow \underset{\textit{stearic acid}}{3HO \cdot CO \cdot C_{17}H_{35}} + \underset{\textit{glycerol}}{C_3H_5(OH)_3}$$

The gradings produced by the commercial process in which the stearic acid is reclaimed from mixed fatty acids by filter-pressing are designated as

single, *double*, and *triple-pressed stearic acid*. The term "saponified" relates to the preparatory process. The term "distilled" relates to the subsequent process of distillation that is customarily resorted to when the crude fatty acids are prepared from grease stocks rich in olein and that would otherwise give a low yield of pressed acid. The by-product of distillation is "red oil" which is a technical grade of oleic acid.

The natural color of saponified grades of stearic acid is pale amber, and this is sometimes preferred by crayon manufacturers and certain others to the whiter distilled grade because of its harder texture.

Greases of tallows may be hydrolysed (saponified) into fatty acids by a number of methods (see Preparation of Waxy Acids). One of the older methods is the Twitchell process, in which the raw stock is boiled in an open vat with sulfuric acid and a catalyzer, known as "Twitchell reagent." The first operation is a washing to remove mechanical impurities, carried out in large wooden tanks equipped with open steam coils. Crude grease is run in, dilute sulfuric acid added, and the mixture is cooked with live steam for 1½ hours. The charge is then run to another steam tank, where the saponification is carried out with the aid of 1 per cent of Twitchell reagent. The stock is boiled for 18 to 20 hours, at the end of which time the "sweet water" containing the glycerol obtained as a by-product is run off.

A so-called second boil follows; the crude fatty acid stock, free from glycerol, is again cooked in the tank employed for the original acid treatment. This additional treatment raises the fatty acid content to around 97–98 per cent. If the grade of grease employed is one requiring distillation to remove excess red oil, the fatty acid mixture from the second boil is transferred to the distilling department; but if the "saponified grade" is being prepared, the charge is sent directly to the storage tanks in the cold-press department. For the customary distillation a stainless steel pot still is used, and operated with superheated steam under vacuum (also see Batch Distillation of Fatty Acids, p. 552). The distillate is a highly refined fatty acid mixture, running a little less than 50 per cent of stearic acid. The residue left in the still is the material known as *stearine pitch*.

The crude fatty acid in the melted state is piped into pans where it is allowed to cool and solidify. The cakes thus formed are wrapped in cloth and pressed in a large hydraulic "cold press." The first pressing requires 2½ hours and produces a low grade material. Further removal of oleic acid is required to produce marketable grades and this is accomplished by hydraulic pressure under elevated temperature conditions. Therefore the cold-pressed acid is melted and again cascaded into pans and formed into cakes, which are wrapped in coarse cloth in preparation for hot pressing. The conditions of operation then govern the grade of the final product.

Triple-pressed stearic acid is stearic acid which has been subjected to two hot presses—the first for 3–3½ minutes, and the second for 5–6 minutes, both with steam of 120 pounds pressure continuously circulating through the press. *Double-pressed* acid has received one hot pressing, which is of relatively long duration. *Single-pressed* acid of standard rubber grade is also one that has been hot-pressed, but differs from the "double" in that the period of hot-pressing is shorter, namely 3 instead of 5 minutes. Each grade will have been melted and boiled with sulfuric acid in a large vat to

improve its color. The product in each instance is drained while hot and finally cascaded into pans which serve as molds to form slabs of finished product.

Single-pressed stearic acid contains about 15 per cent of oleic acid, *double-pressed* 9 per cent, and *triple-pressed* 2 to 4 per cent. All grades contain over 45 per cent of palmitic acid, and less than 3 per cent of myristic acid. Specifications for commercial stearic acid generally include titer, iodine value (Wijs), maximum color Lovibond 5¼" cell, free fatty acid (as per cent oleic), acid value (mg KOH), and saponification value (mg KOH).

USP Stearic Acid. The United States Pharmacopoeia describes a stearic acid which is well suited for pharmaceutical use. A review of the USP specifications will soon show that USP stearic acid contains a very large proportion of palmitic acid. USP stearic acid, or "acidum stearicum," is described as a hard, white or faintly yellowish, somewhat glossy and crystalline solid or a white or yellowish-white powder. The odor and taste are slight, suggesting tallow. Stearic acid is insoluble in water. One gram of USP stearic acid dissolves in 21 ml of ethanol, in 2 ml of chloroform, and in 3 ml of ether, at 25°C. In the tests for purity, the USP states that the congealing temperature should not fall below 54°C (129.2°F), nor the iodine number exceed 4. Tests are also described as to how to detect mineral acid, neutral fat, or paraffine as impurities.

The author determined the melting point of a specimen of USP stearic acid furnished by aleading chemical supply house in New York, as 55.8°C, (132.5°F). The specimen was pure white and had a splendid crystalline structure. It contained 40–45 per cent of palmitic acid. The durometer hardness was 95 at 34°F, and 92 at 82°F. It is of interest to note that the hardness of stearic acid does not vary greatly over a wide range of temperatures. The iodine number was 2.

Analytical Constants of Technical Stearic Acids. Technical grades of stearic acid are referred to as *stearines*. The stearines melt at 52–56°C (125.6–132.8°F); much below the melting point of chemically pure stearic acid. Stearine has a neutralization value of 199–209, and a saponification number of 200–212. These values are appreciably higher than those of the pure acid. Stearine contains a considerable amount of the C_{18} fatty acids, some myristic and oleic acids, and 0.3–0.5 per cent of hydrocarbons. The specific gravity (d^{15}) of stearine is about 0.850; it boils at 383°C; its refractive index (n_D^{80}) is 1.4299.

A *single-pressed* stearic acid has a titer of 52.8–53.3°C, and an iodine number of 9–15. A *double-pressed* stearic acid has a titer of 54–54.5°C, and an iodine number of 7–9. "Emersol 120 Standard Stearic Acid" is equivalent to the double-pressed type. It has a titer of 53.9–54.4°C, iodine number 7.0 maximum, and is of lighter color and more stable to oxidation. A *triple-*

pressed stearic acid is characterized by its relatively high proportion of palmitic acid, its titer, and low iodine number. Because of its similar constants, selective-solvent stearic acids can be substituted for triple-pressed types. "Emersol 130 Lily Stearic Acid" made by the Emersol (selective-solvent) process has the composition palmitic acid 50, stearic acid 48, and oleic acid 2 per cent. The titer is 130.8–131.5°F (54.8–55.3°C); iodine number (Wijs) 1.5–2.5; maximum color (Lovibond-yellow/red) 1.3/0.5–5¼″ cell; free fatty acid (as % oleic) 103–105; acid value 205–210; saponification number 207–212.

"Emersol 140 Palmitic Acid" has the composition palmitic acid 70, myristic acid 1, stearic acid 26, and oleic acid 3.0 per cent. It has a titer of 52.8–55.0°C, a maximum color Lovibond of 2.5/1.0 (yellow/red)–5¼″ cell; a saponification number of 208–214; and iodine number 3.0 maximum.

Vacuum-Distilled Stearic Acid. Armour & Company offers a vacuum-distilled c.p. stearic acid under the designation "Neo-Fat No. 165." This stearic acid has a melting point of about 67°C (152.6°F). The acid contains 90 per cent of stearic, 6 per cent of palmitic, and 4 of oleic acid. It has an iodine number of 3.0 (Wijs), and an unsaponifiable content of 0.5 per cent. A specimen examined by the author had a melting point of 66.7°C (152°F); softening point of 66.7; durometer hardness of 68 at 34°F, 75 at 75°F; and a specific gravity of 0.9088 at 25°/15°C, and 0.9145 at 5°/15°C.

Pure Stearic Acid. The preparation of very pure stearic acid from natural sources presents many difficulties, and hence synthesis must be resorted to. Various methods have been proposed to convert commercial grades of stearic acid to the chemically pure standard; e.g., the addition of a little magnesium acetate to a concentrated alcoholic solution of fatty acids, whereby the salts of the higher fatty acids (stearic acid) which are soluble in alcohol with difficulty are precipitated. Another method is based upon the fractional distillation of the fatty acid esters, particularly the methyl esters which can be rectified under 5 mm absolute pressure; and a third on fractional neutralization with alkalies, the lower fatty acids being neutralized before the higher.

The greater solubility of palmitic acid in ethanol can be taken advantage of to remove palmitic acid, and to prepare a stearic acid of plus 95 per cent purity. In absolute ethanol the solubility of palmitic acid is 31.9 grams per 100 ml, whereas that of stearic acid is 13.8 grams per 100 ml. Ethyl acetate of c.p. grade can be used effectively to separate the acids if the temperature is carefully maintained at 37°C. In this method 350 grams of "double-pressed" stearic acid were dissolved in 350 grams of ethyl acetate in a flask, and the contents of the flask heated to 70°C until all of the stearic acid dissolved. The flask was capped with metal foil and placed overnight in a constant temperature oven set at 37°C. The stearic acid residue was separated from the solvent, drained, and dried. After a melting point determination was made, the residue was again taken up with an equivalent weight of solvent and the process

repeated. Five treatments resulted in a stearic acid which melted at 64°C. The successive melting points were 54.5° (original), 55.5°, 57°, 58°, 59° and 64°C. Further treatment is required to obtain an acid approaching a 69°C melting point.

Hardness of Stearic Acids. For many purposes it is desirable to use a hard grade of stearic acid, even though the melting point is somewhat lower than in the purest grades. Of the fatty acids, oleic and myristic lower the hardness of commercial stearic acid, and palmitic acid greatly increases it. Hence the presence of palmitic acid to the extent of 20–40 per cent or more is not objectionable, provided the oleic acid content is below 4 per cent. The following figures are based upon specimens of stearic acid having 3–4 per cent of oleic acid and varying amounts of palmitic acid, which resulted in almost a straight line curve when durometer hardness was plotted against the percentage of palmitic acid. The data are taken from such a curve.

Percentage of Palmitic Acid	Durometer Hardness at 4.4°C
6	66
10	68
15	70
20	73
25	76
30	80
35	84
40	89
45	94

Myristic acid of 90 per cent purity has a hardness of 54 at 4.4°C. The penetration values (# 14 needle-5 sec/100 g/25°C) of myristic, palmitic, and stearic acids are 24, 16, and 11 respectively. The durometer values at 25°C are 32, 50, and 63 respectively. Palmitic acid has about the same hardness as yellow beeswax, and stearic acid the same hardness as white beeswax.

Eutectics of Palmitic and Stearic Acids. The influence of palmitic acid in depressing the melting point of stearic acid was shown by Heintz[19] as early as 1854. There are apparently two eutectics to such mixtures, one at 50:50 mole per cent of stearic acid and palmitic acid, and the other at 30:70 of the same acids. Lewkowitsch[27] states that a mixture of 47.5 per cent of stearic and 52.5 of palmitic acids behaves as a chemical unit and cannot be resolved into its components by a crystallization from alcohol. The eutectic of the mixed acids has a solidifying point of 54.5°C whereas the pure palmitic acid melts at 62.6° and the stearic acid at 69.3°C. Evidence exists that the eutectic crystal phase may be bimolecular—that is, the palmitic and the stearic acids linked by free hydrogen atoms—and also that the individual acids can to a certain extent be bimolecular.

The melting and solidifying points are given here for the palmitic acid content (0 to 100 per cent) of a mixture of the commercially pure acids.

Percentage of Palmitic Acid	Melting Point (°C)	Solidifying Point (°C)
0	69.2	—
10.0	67.2	62.5
20.0	65.3	60.3
30.0	62.0	59.3
40.0	60.3	56.5
50.0	56.0	55.0
60.0	56.3	54.5
67.5	55.2	54.6
70.0	55.1	54.6
80.0	57.5	53.8
90.0	60.1	54.5
100.0	62.0	—

Uses and Consumption of Stearic Acid. Stearic and palmitic acids are major ingredients in a great variety of products. The major uses of these acids is in physical compounding, reactions involving saponification, and in the chemical synthesis of fatty acid derivatives. The manufacturers of rubber goods, the converters of reclaimed rubber, and the producers of synthetic rubbers are the largest users of stearic acid. The rubber industry consumed 19,084,000 pounds of stearic acid in 1947[23]. These industries use *single-pressed*, *double-pressed*, and *triple-pressed* types of stearic acid in rubber compounding, the type depending upon the grade and usage of the rubber. The function of stearic acid in rubber is to stabilize the cure, activate an accelerator, increase workability, and facilitate mold release.

The second largest user of stearic acid is the candle manufacturer. The consumption of stearic acid in this industry was 7,393,000 pounds in 1944, but declined to 3,711,000 pounds in 1947[23]. Composition candles formerly made of the lower melting paraffins required more stearic acid; today the highest melting paraffins are readily obtainable and require less stearic acid in candlemaking. The compounding of stearic acid in candles, crayons, and buffing bricks is based on its high melting point, its crystallinity, and its waxy nature. The *triple-pressed* type of stearic acid is generally used for such purposes. Palmitic acid is similarly used when extreme hardness is needed. *Commercial palmitic acid* is a 70 per cent palmitic eutectic mixture and has a minimum melting or titer point (52.8–55°C).

The third largest use of stearic acid is the textile industry, which consumes over 2,000,000 pounds per year[23]. Stearic acid is used in preparing the lubricating emulsions used in textile processing. Aside from their use as textile softeners, stearic acid serves as a basic emulsifying and gelling agent in such products as cosmetic creams and lotions, shaving creams,

lubricating greases, wax mixtures, and polishes. The insoluble soaps in the form of the common metallic stearates enjoy a wide usage in many fields, such as cosmetics, lubricating greases, paints, paper, and plastics. Triple-pressed types of stearic acid are used in shaving creams, cosmetics, and pharmaceutical preparations. Color and odor stability are required where stearic or palmitic acids are used in food products. Such qualities are said to be found in the higher grades made by the Emersol process. Stability to oxidation is likewise a requirement of the fatty acid derivatives, such as zinc stearate used in cosmetics.

In 1947 the resin industry consumed 1,782,000 pounds of stearic acid and the trend was upwards. The use of stearic acid in pharmaceuticals has had a downward trend, dropping from 2,676,000 pounds in 1945 to 1,640,000 pounds in 1947. The trend has been slightly down in cosmetics, which industry consumes somewhat less than 2,000,000 pounds. About 2,000,000 pounds of ordinary grades of solid fatty acids are used in core oils. Minor uses of stearic acid are in insulation, metal working, brake linings, artificial leather, adhesives, sulfonation, detergents, polishes, paint and varnish, and soaps[22].

The useful fatty acid derivatives include chlorinated compounds, complex waterproofing compounds, nitriles, amides, amines, ketones, quaternary ammonium salts, and fatty alcohols. The use of stearic and palmitic acids for such purposes has a pronounced upward trend. Also see Polyhydric Alcohol Fatty Acid Esters, p. 534.

Myristic Acid—Technical

Myristic acid is a white waxlike fatty acid which has several industrial applications. In its commercially pure form it has an acid value of 243–249, iodine number 2, unsaponifiable 0.5 per cent, and moisture 0.2 per cent. The melting point (titer) is 48–52°C, as exemplified by "Neo-Fat 13" of Armour and Company. The composition of the "Neo-Fat 13" is 90 per cent myristic, 4 per cent lauric, 4 per cent palmitic acids, and the balance unsaturated acids and unsaponifiables. At 60°C it is soluble in most polar and nonpolar solvents, and is compatible with alkyd resins, asphalt, beeswax, carnauba wax, paraffin, and oils.

Chemically pure myristic may be prepared from commercially pure myristic acid by hydrogenating the latter, whence the unsaturated acid impurities are reduced from 2 to less than 0.2 per cent, and then recrystallizing. This same principle of purification by hydrogenation applies to lauric, palmitic, and stearic acids. A chemically pure myristic acid (53.6°C setting point) may be prepared from butter of nutmeg or from ucuhuba tallow (see p. 291).

The ternary eutectic of freezing points of a mixture of myristic, palmitic,

TABLE 83. COMPARISON OF SYNTHETICALLY PURE AND COMMERCIAL FATTY ACIDS OF HIGH PURITY

	Caprylic Acid $C_7H_{15}COOH$	Capric Acid $C_9H_{19}COOH$	Lauric Acid $C_{11}H_{23}COOH$	Myristic Acid $C_{13}H_{27}COOH$	Palmitic Acid $C_{15}H_{31}COOH$	Stearic Acid $C_{17}H_{35}COOH$
Synthetically pure fatty acids						
Mean molecular weight	144.12	172.15	200.19	228.22	256.25	284.28
Melting point	16.5	31.3	43.6	53.8	62.85	69.9
Iodine value (Wijs)	none	none	none	none	none	none
Neutralization value	389.0	326.0	280.0	246.1	219.0	197.0
Unsaponifiable matter, %	none	none	none	none	none	none
Color	water-white	white	white	white	white	white
New high purity commercial acids						
Mean molecular weight	144.6	172.8	200.8	228.3	258.0	282.5
Melting point	15.0	30.0	42.5	52.0	58.0	67.0
Iodine value (Wijs)	0.8	0.9	0.9	0.9	3.0	3.0
Neutralization value	388.0	324.5	279.5	245.8	216.0	198.0
Unsaponifiable matter, %	trace	0.4	0.3	0.2	0.5	0.5
Color	water-white	white	white	white	white	white

and stearic acids occurs at 42.2°F. It contains 64, 22, and 14 per cent by weight of the respective acids.

The derivatives of myristic acid have many industrial applications. The monoglyceryl ester is a substitute for cocoa butter in suppositories and is used as a superfatting agent for soaps, creams, lotions, etc. in cosmetics. It is also used to some extent in the preparation of agricultural parasiticides. The metallic soaps of myristic acid have industrial uses. Myristic acid is marketed in flake form in both 50-pound multiwall bags and in aluminum tank cars.

Palmitic Acid—Commercially Pure

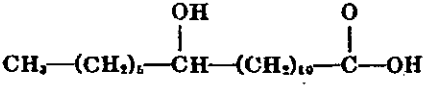
Palmitic acid is a white waxlike acid which is somewhat harder than stearic acid. The demand for palmitic acid of 60 per cent or higher purity is small indeed in comparison with that for stearic acid, and its use in the arts and industries also compares unfavorably.

The chief uses of commercially pure palmitic acid appear to be in buffing compounds, chemical intermediates, cosmetics, emulsifiers, soaps, and metallic coaps. Small amounts of palmitic acid are used in adhesives, belt dressing, candles, cements, crayon, cutting oils, detergents, dry cleaning soaps, duplicating stencils, dyes and dyeing, floor waxes, fruit coating, lubricating grease, metal powders, moistureproofing, paints, pharmaceuticals, plastics, plasticizers, textiles, and wire drawing. Stearic acid, on the other hand, finds a major use for all of the aforesaid purposes.

Lauric acid, the C_{12} fatty acid, is used for pale, uniform alkyds furnished for premium white and pastel nonyellowing high-bake enamels. The enamel may comprise urea or melamine resins and the lauric acid alkyd. The alkyd resin may be prepared from lauric acid ("Neo-Fat 11") 29, phthalic anhydride 42.5, and glycerol 28.5, under a blanket of an inert gas. The mixture is heated to 475°F in 2½ hours, and then cooled to 300°F.

Hydroxystearic Acid

The hydroxystearic acid that has an extensive use is known as 12-hydroxystearic acid, that is, it has an active hydroxyl group (OH) on the twelfth carbon atom.



It is the OH group which changes its physical and chemical properties from those ascribed to stearic acid, and makes it an unique product. In appearance it is a light-tan waxy solid which contains about 85 per cent of pure 12-hydroxystearic acid, and nearly 15 per cent of plain stearic acid. It is soluble in most hot organic solvents. Continued heating of the 12-hydroxy-

stearic acid at temperatures above 100°C lowers the acid value from 182 to 166 (4 hours at 130°C), owing to an intermolecular esterification between the carboxyl (COOH) and hydroxy (OH) groups. The commercial acid has a titer of 73°C (min.), acid value 177–182, saponification number 180–186, iodine number 6.0 (max.)[2].

The chief use of 12-hydroxystearic acid is in lithium-base lubricating greases. The cetyl and stearyl alcohol esters of the acid are also used in greases. (Also see Alkyl Esters of 12-Hydroxystearic Acid, p. 471; and Octadecyl 12-Hydroxystearate, p. 463.) The acid is prepared by hydrolysis of hydrogenated castor oil, which in itself is a high-melting, white, waxy solid (m. 84°C) without odor or taste, and is compatible with a variety of waxes. Hydrogenated castor oil is very hard and is said to have excellent dielectric properties (also see Opalwax and Castorwax, p. 473).

Fatty Acids Synthesized from Hydrocarbon Waxes

In 1946 Bellamy and Nillson[5] reported that in Germany fatty acids had been successfully produced from the paraffins of brown coal. The process of oxidation of the paraffins employs oxygen-enriched air in the presence of a metal catalyst, with certain prescribed temperatures and pressures. The end products include *cupric*, *pelargonic*, *lauric*, *undecanoic*, and other acids containing 13 to 20 carbon atoms. For practical purposes, the acid mixture obtained is freed from water-soluble acid constituents in a washing tower, is separated, saponified with alkali, and the unsaponifiable residues returned to the oxidation reaction vessel. To be commercially profitable a highly efficient plant and management are required.

In the process as it was conducted by the I. G. Farbenindustrie in its several plants, paraffins were obtained from liquite as the source of raw material, and is said to have involved the Fischer-Tropsch synthesis for producing paraffins of high as well as of low molecular weight. The first fraction from the oxidation vessel consists of C_1–C_4 acids and is separated from the gases produced by cooling and absorption in water. The water-insoluble C_5–C_{10} acids are obtained as the first fraction of the vacuum distillation of the less volatile acids. By redistillation the latter can be separated into C_5–C_7, C_7–C_9, and C_9–C_{11} acids. The acids are useful, respectively, as agents in producing "Foamite" type fire extinguishers, flotation of minerals, and for alkyd resins, the latter with pthallic acid as reactant.

The C_{10}–C_{18} fraction separated by distillation under 3 mm pressure is used directly for the production of soaps and edible fats. The C_{18}–C_{24} fraction distilled in the same manner is used largely for making metallic soaps. The distillation residue is used in the manufacture of specialty varnishes, in the preparation of foundry cores, and for the production of the Fischer-Tropsch reaction. Pardun and Kuchinka[33] in 1943 had experi-

mented with a paraffin produced by the Fischer-Tropsch synthesis. They found that the oxidation rate rose to an optimum as the quantity of air used increased and then leveled off during the whole range of temperature in interval from 100 to 160°C.

Equipment Used in Producing Synthetic Fatty Acids

Baldeschwieler[4] describes the process and installation used by the Witten plant, on the Ruhr, of the Deutsche Fattsäurewerke and the Märkische Seifenfabrik for the conversion of the wax (Gatsch) obtained by the Fischer-Tropsch synthesis into edible fatty acids on oxidation, saponification, and vacuum distillation. The oxidation is carried out in 10- to 20-ton aluminum cylinders which have alloy steel heads. Aluminum cylinders are preferred to ones of alloy (Ni, Cr, Fe) steel because of the helpful catalytic action of aluminum. The heads, however, must be made of alloy steel because the volatile acids first driven off from the charge would attack aluminum. Each cylinder is provided with an air-distributing device, a heating coil in the bottom, and a cooling coil about half way up to compensate for the exothermic nature of the reaction. The reaction is stopped when about 30 per cent of the wax has been oxidized. The volatile acids are condensed, absorbed in water, and separated into soluble and nonsoluble acids. The washing towers used for this purpose are about 35 feet high, and are lined with glass.

Saponification of the fatty acids above C_{10} is effected with the theoretical amount of 38 per cent soda, and gives unreacted wax layers, and wax soap emulsion layers. The latter is autoclaved one hour at 170–180°C and 25 atmospheres pressure. Separated wax is returned to the oxidation cylinder, and the lower layer containing 45 per cent soap and 15 per cent wax is charged into the still and heated with gases at 320°C to obtain soap acids and at 380°C to obtain edible acids. The residual wax is returned to the oxidation cylinder. The acids are distilled in the presence of 5 per cent steam. The raw material for the manufacture of edible acids is a middle fraction from the vacuum still and consists of a mixture of C_8–C_{20} acids. The total yield of fatty acids is 80 per cent of the charge put in the still. Edible fatty acids are esterified with synthetic glycerol to yield a triglyceride to which, after purification, vitamins are added.

Fatty Acids from Petroleum Waxes

The fatty acids directly obtainable from the paraffin waxes of petroleum origin are limited to low yield of acids of the desired higher molecular weight (C_{18}–C_{20}) and comprise largely those of an odd number of carbon atoms, not ordinarily found in fats. To secure a higher than ordinary yield, Fischer and Schneider[13] as early as 1919 heated paraffin and dilute solution of so-

dium hydroxide at 170° with air under pressure and a catalyst (Fe, Mn and Cu), and thereby obtained a 95 per cent yield of C_{19}, C_{17}, C_{15}, and C_{13} acids.

In the process of converting paraffins to the fatty acids the wax mass is admixed with the catalyst and subjected to a large volume of air at a prescribed temperature and pressure for a definite period of time, for example 12 hours. After temperature, catalyst, and time, the quantity of air used in relation to the unit mass of paraffins has been recognized as the most important variable, according to the reported investigations of Grün and Ulbrich[18] in 1923, and the later studies made by Pardun and Kuchinka[33] reported twenty years later.

Ellis[11] stated that paraffin waxes of 52–57°C melting point are employed commercially for oxidation at a temperature range of 150–180°C and that the application of increased pressure speeds up the reaction when air is used as the oxidizing reagent. By withdrawing the partially oxidized wax and adding fresh wax to the reaction zone of the oxidation vessel, darkening of the resultant fatty acids may be avoided.

Waxy fatty acids produced with a 52°C melting point wax consist of both fatty and hydroxy acids as well as their anhydrides, lactones, and lactides. The hydroxy acids correspond to the empirical formula $C_nH_{2n}OH \cdot COOH$, where n is an odd number of carbons within the range of C_{13}–C_{19}. The oxidation reactions are aided by catalysts of manganese, Nickel, chromium, and cobalt.

Varlamov[41] in his experiments used 100–200 grams of Grozny-paraffin (m. 52°C) and 500–1000 ml of $2N$ Na_2CO_3, and conducted the oxidation in an iron autoclave at 160–180°C and 15–30 atmospheres pressure for 3–6 hours with air at the rate of 200–400 liters per hour. He found that the rate of oxidation is directly proportional to the pressure, that 20–74 per cent of the paraffin enters into reaction, that dark-colored, insoluble fatty acids amount to 53–78 per cent; the soluble acids are 7–8 per cent, and the hydroxy acids 10 per cent of the oxidized paraffin. The fatty acids had acid numbers of 172–210 and the oxyacids showed an ester number of 66.

As previously stated, only acids of an odd number of carbons were obtained by Fischer and Schneider[13], who identified the acids as *nonadecanoic* (m. 65–66°C), *heptadecanoic* (m. 58–59°C), *pentadecanoic* (m. 50–51°C), and *tridecanoic acid* (m. 38°C). These acids are slightly different from *normal* acids in melting point, and may have a methyl side-chain linkage. These investigators also found that in the absence of water the paraffin in the iron kettle when oxidized with air gives a product which is soluble in hot alkali hydroxide but not in soda, while the acids reprecipitated from the alkaline solution do dissolve in soda, indicating that acid anhydrides, not acids, are formed in the ordinary oxidation of paraffin.

Stearyl Hydroxystearate

Hydroxystearic acid is esterified to produce a stearyl hydroxystearate. The hydroxystearic acid is of the kind described, p. 564, and the stearyl alcohol used in the esterification is one having a melting point of 54–57°C, distillation range of 300–375°C, a hydroxyl number of 215, and an iodine value of less than 2. Stearyl hydroxystearate is a hard wax, tan in color, melting at 69–72°C, viscosity less than 50 centipoises at 75°C. The commercial wax has a specific gravity of 0.900 at 25°C, and 0.839 at 75°C, and a coefficient of expansion similar to that of paraffin wax. Its solubility characteristics are like those of hydroxystearic acid. Although compatible with waxes and resins when hot, it tends to separate on cooling.

Commercial Montanic Acid

Montanic acid, the C_{28} fatty acid, is a hard wax-like solid which melts at 81–82°C. It is prepared commercially in Germany from crude montan wax, although in a form which is quite impure. Salts of montanic acid with heavy metals are prepared by heating the metallic hydroxides or acids with the montanic acid to 140–165°C. The ferrous salt has a congealing point of 88°C, and a drop point of 97°C. When it is heated to 210–250°C it gives the ketone, *montanone*, which congeals at 97°C, and has a refractive index (n^{100}) of 1.4384. When reduced with sodium in ethanol, montanone yields the alcohol, *montanol*, which melts at 97.5°C, and is useful as a nonionic emulsifier. Refluxing of montanic acid with acetic anhydride gives *montanic anhydride* (m. 86°C) which is transformed very slowly to montanic acid on boiling it with water[34].

Equipment for Storage of Fatty Acids

Fatty acids may be handled in aluminum vessels, and in stainless steel (#304), nickel-alloy or glass-lined equipment. For the fatty acids of lower molecular weight (myristic, etc.), "Inconel," "Duramet" alloy, nickel, and stainless steels (types 347 and 316) are employed. Storage of fatty acids in iron, black or galvanized; copper; brass; and most copper alloys is not recommended. Lacquer-lined steel drums appear to be satisfactory.

METALLIC SOAPS

Lithium, the alkaline earths, and the amphoteric and heavy metals form with fatty acids (C_{10}–C_{30}) insoluble salts known as metallic soaps, many of which are of a waxy texture or have waxlike properties. The inorganic bases of these insoluble soaps include lithium, beryllium, magnesium, calcium, strontium, barium; copper, silver; zinc, cadmium, mercury; aluminum, thallium, titanium, zirconium, tin, lead, thorium; antimony, bismuth, chromium, manganese, iron, nickel, and cobalt. The fatty acids include

saturated acids, unsaturated acids such as oleic and erucic, tallic acids (complex from tall oil), and naphthenic acids. This discussion will be confined largely to the stearates, and a few of the lower homologs such as the laurates (C_{12}), myristates (C_{14}), and palmitates (C_{16}); the stearates represent fully 90 per cent of the total production of fatty acid metallic soaps in the United States.

Preparation

The method of preparation of metallic soaps may be *dry* or *wet*. Fourcroy, a contemporary of Lavoisier, gives credit to M. Berthollet who used the wet method for his "ingenious and simple method for the formation of metallic soaps. It consists of pouring a metallic solution into a solution of soap[29]."

In the laboratory wet (or *precipitation*) method, the fatty acid is weighed out and dissolved in hot ethanol, then exactly neutralized with dilute sodium hydroxide in the computed mole weight plus one per cent. The bulk of the ethanol is evaporated off, water added, and the metal salt such as the acetate, in the theoretical amount, is added slowly with stirring. The double decomposition is best conducted at 60°C. The precipitate of metallic soap is allowed to stand and then filtered, washed with water and ethanol, and dried in a spread condition at about 60°C for the laurates and myristates, or at 75°C in a vacuum oven for palmitates, stearates, and higher fatty acid salts.

The technical methods of preparation of the metallic soaps generally utilize steam for melting the fatty acids. After the sodium hydroxide has been added, the temperature is dropped from 90 to 75°C. A separately prepared solution of the metal salt is very slowly added. The slurry formed is kept hot by steam and filtered at 85°C. The precipitated soap is carefully washed free from soluble salts; it is then placed on trays and dried in a vacuum oven. The method is essentially a batch method, although consideration has recently been given to making it a continuous operation. An alternative procedure to the one described is to dissolve the sodium hydroxide in water, heat to 90°C, and pour it into the melted fatty acid while mechanically stirring; the metal salt is then added. The reaction involved is of the following order:

$$\underset{\textit{sodium stearate}}{2C_{17}H_{35}COONa} + \underset{\textit{calcium chloride}}{CaCl_2} \rightarrow \underset{\textit{calcium stearate}}{Ca(C_{17}H_{35}COO)_2} + \underset{\textit{sodium chloride}}{NaCl}$$

The greatest proportion of the total stearates produced commercially is made by the precipitation process. Products so manufactured are of fine particle size, light, and fluffy, and if the metallic soap is a naturally white

one it is of excellent whiteness. In order to avoid discoloration of the metallic soap the materials used in the precipitation process are wood, galvanized iron, rubber, and stainless steel.

In the dry (or *fusion*) method, the fatty acid is heated up in the presence of a metallic oxide, hydroxide, or weakly acidic salt, and the interaction of the metal salt with the fatty acid is brought about at elevated temperatures. In the factory mild steel or stainless reactors, equipped with mechanical stirrers, are employed. The heating of these reactors is controlled thermostatically, so that the water can be driven off at a controlled rate. At completion of the reaction the soap is in the form of a molten mass. The mass is cooled, crushed, pulverized, and classified for the desired size, and packaged. To produce a metallic soap such as calcium stearate the stearic acid is melted with the mole equivalent plus a slight excess of the powdered hydroxide of the metal. When it is necessary to eliminate traces of soluble salts the pulverized material is washed with ethanol and water, dried, and classified for size.

Physical Constants of Metallic Soaps

The metallic soaps of the alkaline metals, namely lithium, calcium, magnesium, strontium, and barium, are ordinarily white crystalline powders, which when fused with heat become plastic, and on cooling congeal to more or less brittle frits. The glassy masses of the magnesium soaps, C_{14}–C_{18}, are yellow, alike in appearance, but differ in hardness. The durometer hardness of *magnesium myristate* is 42, *palmitate* 62, and *stearate* 84, at 25°C. The stearate is quite tough, the palmitate somewhat brittle, and the myristate fragile. *Calcium stearate* is a trifle harder than magnesium stearate. Calcium palmitate is very hard. The laurates and myristates of the alkaline earth metals appear somewhat greasy, whereas the palmitates and higher metallic soaps are distinctly waxy. Many of the heavy metal soaps are highly colored.

The typical properties specified for stearates include total ash content, amount of water-soluble salts, free fatty acid content, moisture content, and fineness. Additional tests, such as solubility and gel strength, are specified for certain end-uses of the stearates in the electrical, rubber, cosmetic, and some other industries. The gel strength obtained with the metal soaps of a balanced combination of acids with C_{14}–C_{22} chain lengths is sometimes superior to that obtained with a single C_{18} chain length. A metal soap of the mixed acids is prepared by using marine base stearic acids[145].

The melting points of the metallic soaps are for the most part indefinite; a few that are well defined are the fatty acid salts of lead, zinc, and mercury. The drop points of most of the metallic soaps are so high, because of the gels they form, that a method such as the "straight tube capillary" must be

resorted to in order to determine the temperature at transition between the solid and fluid state.

The transition of solid-fluid-solid of the metallic soaps involves four stages. In stage *1*, the softening point, gelation begins. In stage *2*, the gelation point, the gelation ends. In stage *3*, the liquefying point (so-called melting point), the gelate liquefies. In stage *4*, the crystal point of Lawrence[26], the gelate crystallizes to a hard solid. The frits obtained from melting powdered soaps, which have been prepared by the wet method, will in many instances melt at a lower temperature than the original powders, possibly because of a smaller unit cell structure.

The Fisher-Johns melting point apparatus affords a means of determining the liquefying point with an accuracy of a fraction of a degree for soaps that have viscous gels. The softening point can also be accurately determined by the Fisher-Johns method.

Soaps of Alkaline Metals

The soaps of the first group of alkaline metals include those of lithium (at. wt. 6.94), sodium (23.00), and potassium (39.01). The melting points of lithium, sodium, and potassium stearates are 136° [28], 180–185°, and 220–260°C respectively. Sodium and potassium soaps, as well as ammonium soaps, are soluble in water. However, the lithium soaps such as lithium stearate are insoluble.

The soaps of the second group, or alkaline earth metals, comprise those of beryllium (at. wt. 9.01), magnesium (24.32), calcium (40.08), strontium (87.63), and barium (137.36). The melting points of beryllium, magnesium, calcium, strontium, and barium stearates are 35°[8a], 107°[42], 140°[42], 145°, and 160°C[29]. It will be noted that in Groups I and II of the metallic soaps there is a rise in the melting point as the atomic weight of the metal is increased for any particular carboxylic acid.

Technical *lithium stearate* is a white powder which melts at 210°C[48] and has a washed ash content of 12.5 per cent. It is insoluble in water, toluene, and mineral spirits. *Lithium lignocerate* melts at 210–218°C.

Beryllium stearate is a white dry powder, which in the mono-form melts at 170°C, and in the di-form melts at 45°C[12]. It is soluble in hot benzene, from which it gels on cooling. *Magnesium stearate*, $Mg(C_{18}H_{35}O_2)_2$, is characteristically a soft and bulky white powder; its smooth bulkiness and efficient covering and bodying action make it widely useful. Magnesium stearate softens at 132° [24] and completely gels at 160°C[42]; the gelate liquefies at 240°C (Lawrence), followed on cooling by a transition to the crystalline state at 109°C[26]. The latter point is similar to the gelation point for magnesium soap prepared directly from magnesium oxide by the fusion method. Jacobson and Holmes[24] gave the gelation points of *magnesium*

laurate, *magnesium myristate*, and *magnesium palmitate* as 150.4°, 131.6°, and 121–122°C respectively.

Calcium stearate prepared by the fusion of calcium oxide with stearic acid has a lower gelation point than that prepared by the precipitation method, possibly owing to a difference in the unit cell structure. The frit of fused calcium stearate has a gelation point of 140°C[44], whereas the softening point of the precipitated calcium stearate is 179–180°C, according to Klimont[25]. The softening points of precipitated *calcium laurate*, *calcium myristate*, and *calcium palmitate* are 100°, 124°, and 144°C respectively. The gelation points of the myristate and palmitate are 150° and 165°C respectively. The frits of calcium myristate and calcium palmitate have gelation points of 74° and 114°C[44]. Calcium myristate in frit form is fragile; the palmitate and stearate show penetration values (100 g/5 sec/25°C) of 5.5 and 13.2 respectively. Calcium stearate is about as hard as paraffin wax of 143–145°F melting point. When powdered, the frit of calcium stearate will sinter at 115–120°C according to Biltz and Röhrs[6]. Technical calcium stearate is a white powder which melts at 150°C[29]. It is soft and very bulky, insoluble in oils and waxes, and inert to solvents; hence its inability to gel. *Strontium stearate* in its commercial form is a white powder which melts at 150–160°C[29], and has a washed ash content of 21.4 per cent. It is insoluble in low molecular weight alcohols and esters. It is partly soluble in and forms gels with aromatic and aliphatic hydrocarbons. *Barium stearate* of chemically pure grade is a white powder which melts at 145°C[12]. It has a specific gravity (d^{15}) of 1.230 and a total metal content of 21.5 per cent. It is insoluble in polar and nonpolar solvents.

Associated with Group I are the soaps of two heavy metals, copper (at. wt. 63.54), and silver (107.88). Whitmore and Lauro[46] describe the colors of the copper soaps as light blue for *copper laurate*, light blue for *copper palmitate*, and pale blue-green for *copper stearate*. *Copper oleate*, a hard crayon-like mass with a fracture-like pitch, has a copper-blue color. The melting points of copper laurate, palmitate, and stearate are given as 111–113°, 120°, and 125°C respectively. As prepared by double decomposition from aqueous-alcoholic solution, using copper acetate and the alkali salt of the fatty acid, the products are fine, fluffy, voluminous powders. Copper laurate is slightly soluble in water, and the palmitate is quite soluble. According to Klimont[25] copper palmitate melts at 138°C.

The melting points of the fatty acid salts of silver in the C_{10}–C_{30} range show a slight decrease as the molecular weight increases. Cheremisinoff[7] gives the softening points as 155–156°, 153–155°, and 135°C. The melting points of the C_{12}, C_{16}, and C_{18} silver soaps were reported by Whitmore and Lauro[46] as above 200°C with decomposition, charring, and emission of vapors. A melting point of 180°C for *silver stearate* by Lawrence[26] appears obvi-

ously too low in view of a more recent one (200°C) by Mansaroff[30a] (see table of melting points). Silver stearate is a fine, fluffy talc-like powder, easily ground, and has no odor. It is very slightly soluble in water and polar solvents. It is soluble in xylene from which it gels; it gives stable gels with petroleum oils.

Associated with Group II are the soaps of three heavy metals, zinc (at. wt. 65.38), cadmium (112.41), and mercury (200.61). *Zinc stearate* is white in color. When pure it melts at 132°C, according to Whitmore and Lauro[46]. The commercial grade melts at 112–117°C, and has a washed ash content of 15.5 per cent. *Cadmium stearate* melts at 104°C[8a]; it is soluble in hot toluene from which it gels on cooling; it is insoluble cold in polar solvents. *Mercury stearate* is a light-green fluffy powder in its precipitated form. When pure it melts at 112.2°[45]; however, the commercial grade melts at a lower temperature, namely 100°C[29]. It is insoluble except to a minute degree in varying solvents.

Soaps of Amphoteric Metals

Metals of the third group, or trivalent amphoteric metals, include aluminum (at. wt. 26.98), gallium (69.72), indium (114.76), cerium (140.13), and thallium (204.39). The technical soaps of Group III are those of aluminum, cerium, and thallium. Since aluminum is trivalent there are theoretically three aluminum stearates which can be prepared from aluminum hydroxide and stearic acid, namely *aluminum monostearate*, $Al(OH)_2(C_{18}H_{35}O_2)$; *aluminum distearate*, $Al(OH)(C_{18}H_{35}O_2)_2$; and *aluminum tristearate*, $Al(C_{18}H_{35}O_2)_3$. The melting points would be roughly 200°, 150°, and 110°C respectively. Actually there is no sharp line of demarcation between the forms of varying valency. Theoretically, the ash content (Al_2O_3) would be 14.81, 8.35, and 5.81 per cent respectively for the three forms of aluminum stearate. Practically, aluminum monostearate has a much lower Al_2O_3 content. The softening points of the stearates prepared from USP stearic acid (45 % palmitic acid) are 160°, 145° and 103°C respectively.

Commercial aluminum stearates are rated according to the total ash, and washed ash, contents. The soluble ash content representing the difference between the total and washed ash is a measure of purity. A high washed ash content points to low free fatty acids and good gelling properties. The Metasap Chemical Company, Harrison, New Jersey[29], lists the total ash contents of its products as 11, 8.6, and 6.6 per cent, and washed ash as 10, 8, and 6 per cent for the mono-, di-, and tristearates of aluminum. The Mallinckrodt Chemical Works lists the following melting points (viscous mass to the near liquid stage) for the technical grades: aluminum monostearate, 190–200°C; aluminum distearate, 155–160°C, similar but "fluffy," 145–150°C; aluminum tristearate, 105–110°C.

The Metasap Chemical Company lists *12-hydroxy aluminum stearate*, $Al(OH)[OOC(CH_2)_{10}CHOH(CH_2)_5CH_3]_2$, with a total ash content of 8.4 per cent and a washed ash content of 7.9 per cent. The theoretical Al_2O_3 content is 7.93 per cent. Technical *aluminum monopalmitate* is harder than the corresponding stearate, and hence is better for polishes, wire drawing, etc. It has a melting point of 180–200°C. *Aluminum monostearate* is soluble or dispersible in nonpolar solvents, oils, and waxes. It resists wetting with water. It takes only 1 or 2 per cent of this soap to harden lubricating grease. *Aluminum distearate* of technical grade melts at 145–160°C, is insoluble in water, lower alcohols, ketones, and esters; slightly soluble in petroleum and aromatic solvents; it is decomposed by boiling methanol or ethanol. It has a pronounced gelling action with oils and greases, and hence is used to thicken them. It is used wherever a high gel strength is needed. *Aluminum tristearate*, like the distearate, is a pale yellow powder. It is slightly soluble cold in acetone, soluble in ethanol but decomposes on boiling, insoluble in ether, and gels with benzene. *Aluminum hydroxystearate* is a white powder which is insoluble in alcohol; it is soluble in toluene yielding a viscous gel; it also yields a rigid gel from mineral spirits and from mineral oil; it yields a thin gel from turpentine.

Thallium stearate appears in small white crystals, which are very slightly soluble in water, acetone, ethanol, and ether. *Thallium laurate* and *thallium myristate* appear as silvery crystals, and *thallium palmitate* as white crystals (see table for melting points). It will be noted that the melting points decrease with increasing weight of the carboxylic radical. *Cerium stearate* consists of white granules which melt at 100–110°C[29]. It is insoluble in water and polar liquids; it is slightly soluble in benzene.

The soaps of the fourth group of metals include those of titanium (at. wt. 47.90), zirconium (91.22), tin (118.70), lead (207.21), and thorium (232.12). The melting points of the stearates of Group IV metals are 62°[26], 60°[8a], 50°[26], 100°[29], and 73°C[26] respectively.

The preparation of divalent and trivalent metallic soaps in either fused or precipitated form has already been outlined. These methods are not applicable to titanium dioxide as this is an extremely inert pigment, nor can a titanium soap be made by mixing hydrous titanium oxide with a free fatty acid and heating under varying conditions. Ryan and Plechner[85a] found that titanium tetrachloride ($TiCl_4$) reacted with fatty acids at moderate temperatures with the elimination of hydrochloric acid (HCl). The reaction is a very rapid one and exothermic.

To prepare *titanium stearate* 500 g stearic acid were heated to 90°C, and 100 g of calcium carbonate were suspended in the melt. To this were added 85 g of $TiCl_4$ in small portions and with vigorous stirring. The reaction mass was heated on a water bath till it was freed from HCl, then cooled, dissolved in 1800 g of ether, and filtered

on a Büchner funnel immersed in ice water to prevent loss of ether. The ether was distilled off and the residue heated under vacuum on a water bath. The product so obtained contained 6.5 per cent TiO_2 and 0.2 per cent chlorine. It melted between 63.5 and 66°C. The melting point is not sharp but clear. The Ryan and Plechner method was found applicable to the preparation of cerium, thorium, zirconium, and aluminum stearates by the reaction of their anhydrous chlorides with stearic acid.

Zirconium stearate is white in color, and the precipitated *tin stearate* is a creamy white powder. In its bivalent form tin stearate has a melting point approaching 105°C, but in the tetravalent form the melting point is only 60°C[8a]. It is soluble in acetone, benzene, and methanol, and in hot heptane from which it gels on cooling. *Lead stearate* is white in color in both the bivalent and tetravalent forms, and is only very slightly soluble in ordinary solvents. Many lead soaps of the saturated fatty acids are known. They have been listed by Piper and his co-workers[22a] as follows: *lead caprylate* 82–82.8°, *caprate* 96.5–97°, *laurate* 103.8–104.2°, *palmitate* 109.6–110.2°, *stearate* 115–115.2°, *cerotate* 112.0–113.5°C. *Lead lignocerate* melts at 117°C[8a]. *Lead 1,10-hydroxystearate* melts at 117–118°C[22a]. Piper *et al.* found that systems composed of liquid paraffin and about 0.5 per cent of lead stearate prepared from stearic acid USP (which is about half palmitic acid) forms a stiff translucent gel when the clear hot sols are cooled.

Metallic Soaps of Heavy Metals of Higher Valency Groups

In the pentavalent group are metallic soaps of nonalkaline or acidic metals, such as antimony (at. wt. 121.76), and bismuth (209.00). In the hexavalent group are the soaps of chromium (52.01), molybdenum (95.95), and tungsten (183.92). In the heptavalent group are the soaps of manganese (54.93). In the eighth group are the soaps of iron (55.85), nickel (58.69), and cobalt (58.94).

Antimony palmitate, $Sb(C_{16}H_{31}O_2)_3$, is described by Nikitina and Maksimova (1949) as a white powder which melts at 84–88°C. *Antimony stearate* melts at 100–106°C. The soaps are soluble only in methanol, and but slightly soluble in benzene, ethanol, and ether[8a]. *Bismuth palmitate* is described by M. Picon (1929)[8a] as of a slightly yellowish color, and as soluble cold in carbon tetrachloride, also benzene, and in soluble hot in ethanol and in ether[8a]. *Chromium stearate* is a green solid, which has a melting point of 95–100°C, according to Licata[23]. The washed ash content of the commercial grade is 8.0 per cent. It is partly soluble in benzene and in mineral spirits.

Manganese stearate is pink in color, and melts at 100–110°C. It has a washed ash content of 13.2 per cent. *Iron stearate* takes the form of a fluffy red-brown powder; it is soluble in light petroleum solvents, but insoluble in the ordinary organic solvents; it does not gel with oils. *Nickel stearate* is olive-green in color. It is soluble hot in polar solvents, but insoluble cold.

TABLE 84. MELTING POINTS OF PURE METALLIC SOAPS (°C)

	Mg	Ca	Ni	Cu	Zn	Hg	Tl	Pb	Ag
C_{12}	82[a]	108.3[a]	77[a]	112[a]	128[a]	100[a]	197[g]	104[h]	212.5[k]
C_{14}	86.8[b]	112[c]	85[c]	116?	128.5[f]	102[c]	181.5[g]	110[a]	211[k]
C_{16}	99[b]	122[c]	96[c]	120[a]	129[a]	105[a]	172[g]	113[a]	209[k]
C_{18}	107[b]	140[b]	100[a]	125[a]	130[a]	112.2[a]	163[d]	115[a]	200[l]
C_{24}	139 ?	156 ?	110 ?	—	134[a]	—	132 ?	117[a]	155[j]
C_{26}	150[a]	160[a]	112[a]	126[a]	138[a]	>115[a]	125[g]	113[h]	
C_{28}	154 ?	—	—	130[f]	—	—	116.5[g]	114 ?	—
C_{30}	160[a]	—	—	135 ?	—	—	—	115.5[a]	180[a]

[a] Melting points by Whitmore and Lauro[46]; [b] by Warth and Hanzely[44]; [c] by Warth and Bulatkin[43]; [d] by Lawrence[6]; [e] by Schwalb, *Ann.*, **235**, 128 (1886)[28]; [f] mean of melting point range of 115–145°C by Presting[34]; [g] melting point by Walter[42]; [h] by Piper *et al.* (1939)[38a]; [i] Tughan and Pink, *J. Chem. Soc.*, **1951**, 1804[80]; [j] by Hell and Hermanns, *Ber.*, **13**, 1713 (1880)[38a]; [k] by Jacobson and Holmes[24]; [l] by Monsaroff[30a].

Note: The melting points given above for magnesium and calcium soaps are gelation points for soaps prepared by the fusion method; similar soaps prepared by precipitation method have higher gelation points.

It is soluble in benzene from which it gels; it gels from petroleum solvents as well. *Cobalt stearate* is purple in color, and in its solubility characteristics is similar to nickel stearate. It melts at 125°C[12]. *Nickel laurate* is bright green in color, although that prepared by Whitmore and Lauro[46] is described as consisting of white crystalline flakes, paraffin-like, greasy, and melted sharply to a clear liquid at 44°C. *Nickel palmitate*, a very light greenish, almost white, powder melted indefinitely near 80°C.

Klimont[25] gives the melting point of *ferric palmitate* as 182°C. Lawrence[26] gives an optimum melting point of 115°C for *ferric stearate*. *Ferrous oleate*, according to Fay and Hamilton[38a], melts at 82°C. Presting[34] has reported on the congealing and melting points for the montanates prepared from technical montanic acid. *Ferrous montanate* congeals at 88°C, and has a drop point of 97°C. *Ferric montanate* congeals at 95°C and has a drop point of 100°C.

Uses of Metallic Soaps

Three of the chief properties which determine the use of a metallic soap are (1) the ability of the soap to dissolve in organic solvents and supply metal cations; (2) the ability to influence the characteristics of liquids in which it is dispersed; (3) the physical characteristics as a whole[10a]. When metallic soap is used in conjunction with paraffin wax the melt is most often in the form of a dispersion rather than a true solution. A small amount of paraffin wax mixed with a metallic soap is generally an aid in securing proper emulsification. Beeswax and lanolin are helpful in securing colloidal dispersions in organic solvents.

Catalysis, fungicidal applications, and glazing are the chief uses of metallic soaps. As wetting and dispersing agents, as extreme pressure agents, as viscosity-adjusting agents, they influence the characteristics of liquids. They also find application as flatting agents and in adjustment of the hardness of organic films.

According to Wendt and Wagner[45] zinc, calcium, and aluminum stearates give "water-repellency" to cements, paper, face powders, and other materials when uniformly distributed in a dry state. Aluminum, barium, calcium, lead, magnesium, and zinc stearates serve as molding release agents during the forming of rubber, plastic, powdered metals, and other materials. Barium and lead soaps are heat-stabilizers for polyvinyl chloride type resins, and cadmium soaps are light stabilizers in the same application.

When *lithium stearate* is added to paraffin it toughens the wax, and raises both its melting point and tensile strength. Lithiated paraffin is dust-repellent, and forms a suitable ingredient with carnauba wax for dry polishes. *Copper stearate* is used in antifouling paints and fungicides. When incorporated in a wax (95 per cent paraffin, 5 per cent microcrystalline) it is useful for treating berry boxes to inhibit mold growth. *Magnesium stearate* because of its smooth bulkiness and efficient covering and bodying action is widely useful. It is used in the manufacture of cosmetics and ointments; in paraffin-oil slushing compositions for lubricating dies used in extruding, molding, and stamping operations; as a flatting agent for varnishes; and as a rubber ingredient. *Calcium stearate* is a trifle harder than magnesium stearate. Its largest use is in high melting point greases as a bodying agent, since it is only slightly soluble in lube oils and does not gel. It is recommended as a releasing agent for the plastic molding industry, and as a flatting agent for paints, varnishes, and lacquers. It is used to some extent in floor polishes, waterproofing fabric, and in crayons. The best of the grades is used to lubricate the metal parts employed in the manufacture of compressed candies. *Strontium stearate* is quite often used in grease and wax compounding. Because of its colored flame it has been suggested for use in pyrotechnic flares and signals[29]. *Barium stearate* has been suggested as a dry lubricant or releasing agent for the plastics molding industry, for wire drawing, and for the preparation of high melting point greases. *Copper palmitate* may be used as the catalyst in the hydrogenolysis of saturated fatty acids in the preparation of fatty alcohols.

Zinc stearate because of its extreme fineness is of much value in cosmetics, and for use in salves and creams. Its relatively low melting point determines its use in plastics and rubber as both an internal and external lubricant. Zinc stearate, *aluminum stearate*, and *beryllium stearate* can be used in the preparation of greases which require stability in a very wide temperature range such as −20 to +240°C. To prepare the grease the metallic soap in

its freshly precipitated state can be mixed with the lube oil to produce a gel, and the grease washed free from salts and heated to 125°C to remove traces of water. Since zinc stearate is insoluble in organic solvents at low temperatures, and thus lacks gelling power, it makes a good flatting agent for varnish and nitrocellulose lacquer. Its good filling properties makes zinc stearate suitable for "sanding sealers." *Zinc palmitate*, which melts at a lower temperature than the stearate and is of a higher specific gravity, is used in preference for some types of lacquers, and as a pigment suspending agent in luminescent paints. *Mercury stearate* is used in a medicinal ointment.

Aluminum palmitate is more soluble in hydrocarbon solvents than aluminum stearate and forms heavier gels at lower temperatures, making it useful in a particular place where the range of heat is limited. A suggested use is as a thickening and suspending agent in paints and inks. *Aluminum monostearate* is used where exceptionally heavy bodying properties are desired in the manufacture of paints, inks, greases, and waxes. Aluminum distearate is the most commonly used grade of the aluminum soaps. It has a pronounced gelling action with oils and greases and hence is used to thicken them. It is also used as a flatting agent for paints and varnishes, as a waterproofing agent for paper, textile fabrics, rope, and masonry, or wherever a high gel strength is needed. *Aluminum tristearate* is used where thin gels are required. As an ingredient (2–3%) of putty oil it prevents bleeding and separation of the oil from the solids in canned putty. *Aluminum hydroxystearate* may be used to advantage in paints and inks, but not in nitrocellulose lacquers because of its solubility in alcohols and esters. It is used in the treatment of leather and cement to provide waterproofness. It is applied as a lubricant to rope and plastics.

Wendt and Wagner[45] give the 1952 production of aluminum stearate as 8,735,000 lb, zinc stearate 5,429,000 lb, calcium stearate 3,763,000 lb, lead stearate 1,302,000 lb, all other stearates 2,376,000 lb.

Cerium stearate has been suggested as a catalyst because of its relatively high metal content. It is of waxy texture and miscible with waxes. *Titanium stearate* suspends the pigment in paint better than aluminum stearate, and thus avoids hard-settling. *Zirconium stearate* may be used to retard the chalking of paints that contain titanium dioxide pigment. *Lead stearate* may be used in greases, waxes, and paints wherever the incorporation of an organic lead compound would be advantageous. It has a specific gravity (d^{15}) of 1.323. It introduces both lubricating and heat stabilizing properties into vinyl compounds. *Lead stearate* is used for control of burning rate in ammunition powders. *Chromium stearate* is used as a catalyst, as a source of organometallic chromium, and as a leather waterproofing agent. Like zirconium stearate, it is used to retard the chalking of titanium

dioxide paints. Owing to its green color, chromium stearate has possible application in coloring waxes, greases, plastics, coatings, and ceramics[29].

Manganese stearate is easily dispersible in hydrocarbons, and may prove useful as a catalyst. *Nickel stearate* may be used as a catalyst in oxidation and polymerization reactions. It is used for the treatment of leather, as a detergent in organic liquids, and as a powdered quench in nickel welding. *Cobalt stearate* is useful as a catalyst in the Oxo process for the production of high molecular weight alcohols. *Ferric stearate* is used to some extent as a catalyst in polymerization, e.g., polymerization of styrene in solution, although the metallic oleates of zinc, magnesium, cobalt, nickel, and iron are more effective, more or less in the order here stated.

Plastigels

Plastigels are essentially vinyl plastisols; that is vinyl resin, plasticizer, and pre-gel are milled together. The best gelling agents appear to be sodium stearate, calcium stearate, lithium hydroxystearate, and magnesium, strontium, and lithium stearates. The use of metallic soaps in plastigels takes advantage not only of their efficiency as gelling agents, but also of their stabilizing properties. Some of the plastigels discolor on fusing; that prepared from lithium hydroxystearate is reported to show the best clarity of fusion.

Waterproofing Lubricating Greases

Zinc, cadmium, and magnesium 12-hydroxystearates have received consideration in the waterproofing of lubricating greases. *Zinc hydroxystearate* may be prepared by heating *12-hydroxystearic acid* with water to near boiling, stirring in a hot solution of sodium hydroxide, and then adding a solution of zinc sulfate. After an hours' agitation the water is withdrawn from the bottom; the zinc hydroxystearate is washed twice with warm water, and then dried in shallow pans. For further details of preparation consult U. S. Patent 2,445,936 (1948) granted to Butcosk for the waterproofing of lubricating greases.

References

1. Anonymous, Armour & Company, Research Labs. publication (1944).
2. Anonymous, Emery Industries, Inc., "Emery Solid Fatty Acids," publication (1950).
3. Axelrad, S., and Hochstadter, F., *Ind. Eng. Chem.*, **9**, 1123–1125 (1917); U. S. Patent 1,291,384 (1919).
4. Baldeschwieler, E. L., *Chimie & industrie*, **55**, 329–330 (1946).
5. Bellamy, L. J., and Nillson, K. T., *Chimie & industrie*, **56**, 18 (1946).
6. Biltz, W., and Röhrs, W., *Z. angew. Chem.*, **36**, 609–611 (1923).
6a. Breuer, F. W., and Zentmeyer (Armstrong Cork Co.), U. S. Patent 2,646, 436 (1953).

7. Cheremisinoff, P. N., *J. Am. Oil Chemists' Soc.*, **28**, 278–279 (1951).
8. Delcourt, Y., *Bull. soc. chim. Belg.*, **40**, 284–294 (1931).
8a. Doss, M. P., "Properties of the Principal Fats, Fatty Oils, Waxes, Fatty Acids and their Salts," publication by the Texas Company, New York (1952).
9. Dutton, W. C., U. S. Patent 2,198,991 (1940).
10. Eisenlohr, G. W. (M. Werck & Co.), U. S. Patent Reissue 22,006 (1942).
10a. Elliott, S. B., *Am. Paint J.*, **26**, No. 35, 50, 52, 54 (1942).
11. Ellis, C., "The Chemistry of the Petroleum Derivatives," Vol. 2, New York, Reinhold Publishing Corp., 1937.
12. "Encyclopedia of Chemical Technology," edited by Kirk and Othmer, New York, Interscience, Inc., 1951.
13. Fischer, F., and Schneider, W., *Ber.*, **53B**, 922–925 (1920).
14. Flaxman, M. T., U. S. Patent 2,127,490 (1938).
15. Friedolsheim, A. v., and Luther, M. (I. G. Farbenind., A.G.), U. S. Patent 1,990,229 (1935).
16. Friedrich, H., German Patent 674,874 (1939).
17. Griesinger, W. K., U. S. Patent 2,238,109 (1941).
18. Grün, A., and Ulbrich, E., *Z. angew. Chem.*, **26**, 125–126 (1923).
19. Heintz, W., *Ber. Akad. Weis., Berlin*, **1854**, 207–213; *J. Prakt. Chem.*, **63**, 168–169 (1854); *ibid.*, **66**, 1 (1855).
20. Hilfer, H., *Drug & Cosmetic Ind.*, **72**, No. 8, 38 (1953).
21. Howe, I. S., *Trans. Rev. Soc. Canada*, **12**, iii, 13–18 (1918).
22. I. G. Farbenindustrie, A.G., British Patent 304,150 (1928).
23. Industry Division, "Fats and Oils, 1943–1947," Bureau of Census, Department of Commerce, Washington, D. C., 1948, p. 48.
23a. Ittner, M. H. (Colgate-Palmolive-Peet Co.), U. S. Patent Reissue 22,006 (1942).
24. Jacobson, C. A., and Holmes, A., *J. Biol. Chem.*, **25**, 29 (1916).
25. Klimont, J., *J. prakt. Chem.*, **109**, 265–272 (1925).
25a. Kuhrt, N. H., *et al.*, *J. Am. Chem. Soc.*, **27**, 310–313 (1950).
26. Lawrence, A. S. C., *Trans. Faraday Soc.*, **34**, 660–667 (1938).
26a. Leader, W. M., U. S. Patent 2,567,541 (1951).
27. Lewkowitsch, J., "Chemical Technology of Oils, Fats and Waxes," 5th Ed., Vol. 1, p. 116, London, Macmillan & Co., Ltd., 1915.
28. *Ibid.*, p. 167.
29. Metasap Chemical Company, publ. "Metallic Soaps," Harrison, New Jersey, Revised Ed., 1948.
30. Mills, V. (to Procter and Gamble Mfg. Co.), U. S. Patent 2,156,863 (1939).
30a. Mansaroff, A., *Can. Chem. Process Ind.*, **26**, 193–196 (1942).
31. Muller, O. F., U. S. Patent 2,140,759 (1939).
32. Noncle, M. G. G., French Patent 837,418 (1939).
33. Pardun, H., and Kuchinka, R., *Petroleum Refiner*, **22**, 410–414 (1943).
33a. Piper, J. D., *et al.*, *Ind. Eng. Chem.*, **31**, 307–317 (1939).
34. Presting, W. (VVW Kohlewertstoffe, Halle [Saale]), *Chem. Tech.* **4**, 152–156 (1952).
35. Rubinshtein, V., *et al.*, *Maslobeĭno Zirovoe Delo. U.S.S.R.*, **12**, 254–255 (1936); Russian Patent 46,660 (1936); [*Chem. Abstracts*, **30**, 7372 (1936), **33**, 3620 (1939)].
35a. Ryan, L. W., and Plechner, W. W., *Ind. Eng. Chem.*, **26**, 909–910 (1934).
36. Sayre, J. E., and Marsel, C. J., *Chemical Week*, **71**, No. 18, 29–50 (1952).
37. Standard Oil Development Co., British Patent 637,389 (1950).
38. Steinberger, S. (to The Richards Chemical Works), U. S. Patent 2,506,473 (1950).

39. Stingley, D. V., *Chem. Ind.*, **48**, 50–52 (1941).
40. ——, *et al.*, *Ind. Eng. Chem.*, **42**, 202–213 (1950).
41. Varlamov, V., *Maslobo˘no-Zhirovoe Delo*, **1932**, No. 7, 39–43.
42. Walter, Robt., *Ber.*, **59-B**, 962–972 (1926).
43. Warth, A. H., and Bulatkin, I. F., in 1st Ed. of Warth, "The Chemistry and Technology of Waxes," 1947.
44. ——, and Hanzely, E. M., *ibid.*
45. Wendt, R. E., and Wagner, E. F., *J. Am. Oil Chemists' Soc.*, **21**, 590–593 (1954).
46. Whitmore, W. F., and Lauro, M., *Ind. Eng. Chem.*, **22**, 646–648 (1930).
47. Wilson, G. R., *J. Am. Oil Chemists' Soc.*, **31**, 564–568 (1954).

9. Methods for Determining the Constants of Waxes

DETERMINATION OF CHEMICAL CONSTANTS

Significance of Chemical Constants

Chemical constants such as acid, ester, hydroxyl, and iodine numbers are determined to identify, differentiate, or classify the waxes, particularly lipid waxes. The *saponification number* is a direct evaluation of the total amount of esters plus free acids, if any, in a wax which is free from polyesters and resins. It approaches a constant number for the particular kind of refined wax. The term *saponification value* is used synonymously with Köttstorfer number for vegetable oils which are essentially glycerides, or for waxes having simple esters. The term "number" is also used to express the value of a specific constituent in a fat or wax.

The *acid value* expresses the free fatty (or waxy) acid, and is more of a variable than the saponification number. The *ester value* is generally regarded as the difference between the saponification number and the acid value. It is quite often, but not always, a measure of the amount of ethers or esters in the wax.

When a single acid constituent of a wax is considered, where the acid and saponification number are substantially the same thing, as for example commercial stearic acid, the amount of alkali (KOH) required to effect neutralization is referred to as its *neutralization number*. The *acid equivalent* is the amount of acid required to neutralize a unit equivalent of alkali.

$$\text{Acid equivalent} = \frac{56{,}104}{\text{neutr. number}}$$

The neutralization number of a pure acid can be calculated if the formula of the acid is known. For example, ursolic acid has the formula $C_{29}H_{45}(OH) \cdot COOH$, and hence its molecular weight is 456.68. Therefore its neutralization number is 56,104/456.68 = 122.85.

A specimen of commercial ursolic acid had a neutralization of 121.5 and a saponification number of 123.5 by actual analysis. The *neutralization equivalent* would be 56,104/121.5 = 461.73 which is a rough approximation of its molecular weight. The indicated purity of the commercial ursolic acid would

be 121.5/122.85 × 100 = 98.9 per cent. The difference between the neutralization and saponification numbers, namely 2.0, would indicate the presence of nonacid saponifiable material as an impurity.

The *nonsaponifiable matter*, or unsaponifiable material, sometimes referred to as unsaponifiable, is an important determination in the identification of a wax, or in the study of its composition. It includes not only the unsaponifiable portion of wax such as the combined alcohols, split off from the ethers or esters as a result of saponification, but also *hydrocarbons* and *free alcohols*, and *ketones*, if any. Alcohols include sterols, if any, as well as aliphatic alcohols.

The percentage of total fatty or wax acids is approximately the difference between the percentage of nonsaponifiable matter and 100 per cent. Combined acids are total acids less free acids (inclusive of resin acids). The percentage of esters usually varies from 2 to 2.6 times the amount of combined acids found in the wax. The chemical constants assist greatly in determining the chemical composition of the wax once the individual constituents are recognized by molecular weight, melting point, and other determinations.

The principles involved in elucidating the chemical composition of a lipid wax (natural wax ester) lie in ascertaining (1) the amounts of acid and alcohol components, and their molecular weights and melting points; (2) the degree of unsaturation of both the acid and alcohol components; (3) the amount of hydroxyl groups in the acids component; (4) the degradation of the esters into simple esters, hydroxy esters, acid esters, and diesters through the agency of functional group analysis and fractionation by molecular distillation; (5) the amount of nonacidic material found in the acid fraction as a measure of the amount of lactones; (6) the amount of free acid and its separation from resin acids; (7) the amount of hydrocarbons in the unsaponifiables. To identify the various components it is necessary to resort not only to chemical constants but to physical constants as well.

The chemical constants customarily reported for a wax may be grouped as follows: (1) saponification number, and occasionally the Hehner number and Reichert-Meissl number; (2) halogen absorption number, usually Hübl, Hanus, or Wijs iodine numbers; (3) acetyl number and/or hydroxyl number as a measure of hydroxyl groups of alcohols, hydroxy acids, and sterols; (4) acid value, and indirectly ester value as the difference between the acid value and saponification number; (5) the amount (%) of total fatty acids separated by HCl hydrolysis of the soaps obtained by saponification; (6) the amount (%) of unsaponifiable material.

Chemical tests other than those mentioned above are sometimes made for the identification of the constituents of wax, e.g., tests for : (1) thiocyanogen (CNS_2) absorption and the formation of crystalline bromo-addition pro-

ducts; (2) the proportion of water-soluble or -insoluble volatile fatty acids present; (3) the analysis of small amounts of glycerol; (4) the separation of small amounts of resins; (5) the presence of sterols and triterpene alcohols (relative quantity, if possible); (6) the presence of lactones (quantity, if possible); (7) the presence of mineral matter, and whether it is free or combined.

Saponification Number. The saponification number is the number of milligrams (mg) of potassium hydroxide (KOH) required to hydrolyse one gram (1 g) of the wax or waxy material.

The determination of the saponification number of a wax follows the procedure of an oil, except that the solvent selected for the purpose must be one that will keep the unsaponifiable portion in a state of solution, and hence for some waxes alcohol of 96 per cent strength, or even absolute alcohol, cannot be safely used.

For the ordinary determination of the saponification number it is customary to take 2 to 5 g of sample, and insert this in a 250 to 300 ml flask containing 30 ml of absolute alcohol. Alcoholic KOH (50 ml of approximately half-normal, or 25 ml of approximately normal) is run from a burette with constant stirring at a steady rate, say for 2 minutes. The contents of the flask is gently boiled with occasional thorough shaking for at least one hour after the solution starts boiling, under a reflux or air condenser, plugged at the top with glass wool. The excess of KOH is titrated with half-normal ($0.5N$) or tenth-normal ($0.1N$) hydrochloric acid (HCl). In addition to phenolphthalein as an indicator it is a good plan to add 1 ml of methylene blue (.01 per cent strength) so that the end point is more sharply distinguished by transition from a brownish-purple or bluish-purple to a clear pale or dark green color.

Converting the normality of the HCl to that of normal KOH,

$$\text{saponification number} = \frac{V_b - V_w \times 56.104}{w}$$

where w = weight of sample taken, and V_b, V_w are respectively the number of milliliters of normal HCl used in the blank and the actual analysis.

Aromatic solvents other than toluene have been recommended by investigators. Marcusson[19] preferred to use benzene with montan wax. Berg[4] preferred to use xylene with carnauba wax. Berg's method specifies that 4 g of the wax sample are dissolved in 20 ml of xylene, than 50 ml of $0.5N$ alcoholic KOH are added and the solution boiled for 2 hours under a reflux condenser. Next, 100 ml of alcohol are added and the solution titrated with $0.5N$ HCl. Berg found this procedure more effective than boiling for 8 hours or more with alcohol as the solvent. A modification of the Berg method is in use for determining the acid and saponification values of carnauba and

other waxes, namely: Boil 4 g of wax with 20 ml of absolute alcohol for 5 to 10 minutes with reflux, and titrate the hot liquid at once with 0.5*N* NaOH for acid value. Add 50 ml of 0.5*N* alcoholic KOH, boil for 30 minutes, add 75 ml of 96 per cent alcohol, heat 5 minutes, titrate with 0.5*N* HCl, boil 3 minutes, and again titrate until colorless for saponification number.

In determining the saponification number of beeswax a more concentrated solution of KOH has been favored, and an extension of the time of saponification; e.g., 3.5 g of wax are dissolved in a minimum of absolute alcohol, 35 ml of 0.7 KOH are added, and the saponification is carried out for 3 hours. The presence in beeswax, carnauba wax, caranda wax, candelilla wax, etc. of hydroxylated esters make complete saponification more difficult than when the wax is comprised of simple esters. Findley and Brown (1953)[7] dissolved such waxes in warm pure toluene, as was first proposed by Wand (1939)[28]. Wand preferred toluene as a solvent for waxes because of its great solvent power and its miscibility with alcohol.

The Wand procedure is as follows: Place 2 g of the wax in a dry 250-ml Erlenmeyer flask. Measure in exactly 10 ml of pure toluene. Warm gently on a hot plate until wax dissolves but do not boil. Now run in from a pipette 25 ml of 0.7*N* alcoholic KOH (approximately 39 g of KOH per liter). At this point some of the dissolved wax may precipitate but it will redissolve when the flask is warmed. A blank determination is run by measuring the same amounts of toluene and reagent in a second flask. Place both flasks under reflux condensers and hold at a gentle boil for 2 hours, to complete the saponification. Now add 5 to 6 drops of phenolphthalein indicator and titrate to complete disappearance of pink. The blank, containing 25 ml of alcoholic KOH, will require 35 ml of 0.5*N* HCl. The difference between the blank and the sample measures the amount of KOH consumed in the saponification. One ml of 0.5*N* HCl is equivalent to 28.06 mg of KOH.

Use of polar solvents. A number of polar solvents other than ethanol have been proposed for use in determining saponification numbers. In the Winkler[30] method of saponification of waxes as recommended by that author in 1911, and the value of which was confirmed by Andre and Maille[1] in 1947, propanol is used instead of ethanol in making up the alcoholic KOH solution. Propanol is a good solvent for most waxes, and since it has a higher boiling point than ethanol, the saponification proceeds faster, and no reflux condenser is required. With methanol the saponification was slow and incomplete, and with butanol there is color and immiscibility interference during the back titration of KOH. Amyl alcohol (pentanol) can be used to advantage where it happens to be a formidable solvent for the end products of saponification that cannot otherwise be kept in solution. Isopropyl alcohol (isopropanol) may be used in place of amyl alcohol.

Ethylene glycol when used in place of ethanol as proposed by Hezel yields

higher saponification numbers, as has been confirmed by Zöllner[31]. The relatively new Hezel method may be briefly described as follows: 3–5 g of test wax sample is heated with 40–50 ml of approximately 0.5*N* KOH solution in ethylene glycol in a covered 250-ml Florence flask which is placed inside an oven; a little xylene can be added to make the mixture fully soluble. (See Appendix for saponification numbers of waxes by the Hezel method.) This method has not yet been recognized as a standard procedure for general use; it does seem to throw some light on the complexities of the ester composition of waxes.

Saponification Equivalent. The saponification equivalent is the amount of fat or wax saponified by one gram-equivalent of KOH, and is therefore the mean gram-equivalent of the mixture of glycerides or of wax esters, as the case may be, in the material examined, on the assumption that the latter consists of neutral and not acid types. For simple wax esters,

$$\text{saponification equivalent} = \frac{1000w}{v_b - v_w}$$

from which equation and that of saponification number previously cited may be deduced the expression,

$$\text{saponification equivalent} = \frac{56{,}104}{\text{sapon. number}}$$

Acid Value. The acid value (acid number) is the number of milligrams of KOH required to neutralize 1 gram of the wax or waxy material.

The standard practice is to determine the acid value by warming 4 to 5 g of the wax with 50 ml of carefully neutralized alcohol in a 250-ml Erlenmeyer flask. A few drops of phenolphthalein are added and the titration is made with vigorous shaking against a solution of approximately 0.1*N* alcoholic KOH until a semi-pink color appears. A blank should be run at the same time and the titration if any deducted from that on the sample.

$$\text{Acid value} = \frac{v_w \times 56.104}{w}$$

$$\text{Free waxy acid } \% = \frac{\text{acid val.} \times M}{561.04}$$

where M = mean molecular weight (m. wt.) of waxy acid.

As the higher molecular weight waxy constituents are not particularly soluble in alcohol, it may be necessary with some waxes to resort to one of the following solvents: (a) equal parts of methanol and toluene, (b) 1 part of ethanol and 2 parts of light petroleum spirit (boiling point about 80°C); (c) amyl alcohol or isopropyl alcohol.

There are instances where it is preferable to attach a reflux condenser to

the flask and freely boil the solution for not more than 2 minutes before titrating. The blank should be boiled for exactly the same length of time.

Ester Value. The ester value is the difference between the saponification number and the acid value, and therefore shows the amount alkali consumed in the saponification of the esters.

If the wax is free from polyhydric alcohol esters the

$$\% \text{ esters} = \frac{\text{ester value} \times M}{561.04}$$

where M is the mean molecular weight of the esters.

If the esters are acids combined with glycols the

$$\% \text{ esters} = \frac{\text{ester value} \times M}{561.04 \times 2}$$

If the esters are glycerides as in bayberry wax then

$$\% \text{ esters} = \frac{\text{ester value} \times M}{561.4 \times 3}$$

Estimate of Esters. The percentage of esters in a wax can be roughly estimated provided the nature of the principal ester constituent is known and whether it is a simple ester, or contains diesters. For example, the refined wax of the candelilla plant had a mean ester value of 37.7. Its chief constituents had a molecular weight of 510. The factor for converting ester value to per cent of esters in this case would be 510/561 or 0.91. Since the candelilla wax had an ester value of 37.7, the per cent of esters would be 37.7 × 0.91, or 34.3. Since the lactones plus free acids plus hydrocarbons amount to 66 per cent, the esters by difference amount to 34 per cent, in close agreement with the calculated value. Candelilla wax contains no diesters.

The principal constituent of beeswax is myricyl palmitate which has a molecular weight of 663. The factor for converting ester value to per cent of esters would be 663/561 or 1.182. Since beeswax has an ester value of about 73, the per cent of esters would be 73 × 1.182, or 86.3. The percentage of esters in beeswax is known to be only 72, therefore its relatively high ester value must be attributed to the presence of diesters; triesters are known to be absent. Beeswax is known to contain 6 per cent of diesters.

Carnauba wax has esters having a mean molecular weight of 775. The factor for converting ester value to per cent of esters would be 775/561 or 1.4. Since carnauba wax has an actual ester value of 75, the percentage of esters would be 75 × 1.4 = 105. Since this abnormally high calculated percentage contrasts with the actual percentage (100 less hydrocarbons, free acids, and free alcohols) which is but 85, the relatively high ester value of 75 must be attributed to ester values much higher than normal, namely diesters. Carnauba wax is now known to contain about 20 per cent of diesters.

Taking 807.29 (m. wt. palmitin) as the mean molecular weight of the run of glycerides the percentage of glycerides is roughly 0.48 × ester value. For example, bayberry wax has an ester value of 210; 210 × 0.48 = 100.8 per cent. The actual amount of glycerides is 97 per cent. This would indicate the presence of a glyceride of lower molecular weight, which happens to be myristin (m. wt. 723.14).

To determine the ester value directly, proceed as follows: Shake 2 grams of the pulverized wax, accurately weighed in a 200–250 cc tared flask, with 20–30 ml of neutralized alcohol, add 1 ml of phenolphthalein indicator, and titrate with half-normal alcoholic potassium hydroxide until the free acid is neutralized. Add exactly 25 ml of half-normal potassium hydroxide, and proceed as directed under saponification number, beginning with gentle boiling. The ester value is computed by substituting "ester value" for "saponification number" in the equation.

Iodine Number. The *iodine number* or "iodine absorption value" expresses the percentage of iodine (at. wt. 126.92) that is absorbed by the wax when treated with a suitable solution of iodine. It indicates the amount of unsaturated fat or wax acids, unsaturated esters, unsaturated hydrocarbons, and unsaturated alcohols inclusive of sterols and resins. Each double bond requires two atoms of iodine.

The iodine number is determined with a "carrier" for the iodine, in which case the solution may be iodine monochloride in glacial acetic acid (Wijs); iodine monobromide in glacial acetic acid (Hanus); or iodine-mercuric chloride in alcohol (Hübl). The unadsorbed iodine is titrated with standard tenth-normal (1/10*N*) sodium thiosulfate. Other reagents required in the test are potassium iodide solution (10 per cent) and dry chloroform or carbon tetrachloride.

Wijs solution can be prepared by one of two methods, the first more rapid and the second less expensive in materials.

(1) Iodine trichloride (7.8 g) and iodine (8.5 g) are dissolved in warm glacial acetic acid (HA) and made up to 1000 cc with glacial HA in the cold; or

(2) Iodine (13 g) is dissolved in a liter of glacial HA and pure dry chlorine (Cl) gas is passed through the solution until its titration number to thiosulfate is exactly doubled:

$$I_2 + Cl_2 = 2\,ICl$$

Hanus solution is prepared by dissolving together 13.2 g of iodine and 8 g of bromine in a liter of glacial HA.

Hübl solution: (a) Iodine (25 g) is dissolved in 500 cc of 95 per cent ethanol; (b) mercuric chloride (30 g) is dissolved in 500 cc of 95 per cent ethanol. The reagent is made up by taking an equal volume of (a) and (b) when needed.

For Wijs, Hübl, or Hanus solutions:

$$\% \text{ Iodine absorption} = \frac{(V_b - V_w)}{w} \times 1.27$$

where w is the weight of wax, and V_b, V_w are the respective number of milliliters of thiosulfate solution (reckoned as tenth-normal) used in the blank and actual analysis.

To determine iodine number by the *Hübl method*, weigh out an amount of sample which will absorb 0.3–0.4 gram of iodine; place this in a clean dry flask and add 10 cc of chloroform. When the sample has completely dissolved, add 25–30 cc of the mixed iodine solution, and stopper the flask carefully. Fill the gutter around the stopper with potassium iodide solution to guard against loss of iodine. Shake flask gently and set aside for 3 hours or more in a dark closet. Run blank in a similar dry flask using the same amounts of chloroform, iodine solution, and potassium iodide. Add 100 cc distilled water to each flask and 20 cc of potassium iodide solution. Titrate the excess of iodine at once by means of the standard thiosulfate solution.

Attempts have been made to modify the existing methods so as not only to shorten the time of the determination to a matter of minutes but to secure the optimum halogen absorption under all circumstances, and the most reliable iodine numbers.

Method of Benham and Klee[3]. In the Rosemund-Kuhnheim procedure as modified by Benham and Klee, the reagent is made up of (a) 40 ml of c.p. glacial acetic acid to which 28.5 g of c.p. pyridene are added; (b) 28.4 g of concentrated sulfuric acid; (c) 1 oz bottle of c.p. bromine (28.35 g). When cool, add contents of second flask (b) to contents of first flask (a); then add contents of third flask (c) to the mixture of (a) and (b), and make up whole to one liter with c.p. glacial acetic acid. Mix, transfer to a 4-liter screw stoppered bottle, and add 2500 ml of c.p. glacial acetic acid, making a total of 3500 ml of reagent. The reagent is approximately tenth normal (0.1N) with respect to bromine.

The mercuric acetate is made up in 2.5 per cent strength in glacial acetic acid, and 10 ml is added to 50 ml of the R-K reagent, previously added to the wax in carbon tetrachloride. The absorption time is fixed at one minute in diffused light and employing 125–150 ml excess of reagent.

Unsaponifiable Matter. Under the term *unsaponifiable matter* (non-saponifiable residue or fraction) is included all substances that cannot be changed to water-soluble products by the process of saponification. It can readily be separated by ether extraction from the soap solution resulting in the saponification of the fat, or wax.

The products which are found in the unsaponifiable fraction consist of the higher alcohols, including the sterols; the fat-soluble vitamins A, D, and

E; carotenoids; and hydrocarbons. Generally speaking, no more than traces of vitamins and carotenoids, if any, are encountered in waxes.

Vitamin D itself is a wax since it is an ester of 7-dehydrocholesterol. The carotenoids (α and β carotene) are basically unsaturated hydrocarbons of about 40 carbons having methylated six-member rings, one at each end of the hydrocarbon chain, and include associated natural pigments giving color to the oil, fat, or wax as the case may be.

In determining the unsaponifiable material, the alcohol of the saponifying agent is distilled off from the saponified sample and the residue taken up in about 200 ml of water and placed in a 500-ml separator; ether (200 ml) is added, and the whole shaken gently with a swirling motion. If undue emulsion forms, a few drops of alcohol and/or brine should be added. The aqueous layer is extracted twice with fresh ether. The ether extracts are combined and washed once with water to remove traces of soap; then concentred by heating in a tared flask in a steam-oven until the weight is constant.

Total Acids and Unsaponifiables. In a note on the saponification of carnauba wax, Findley and Brown[7] call attention to the fact that the quantitative separation and determination of unsaponifiable material and acids in a wax usually require two quantitative transfers of dried materials, one of the dried saponification residue to the extractor, the other from the extraction thimble prior to acidification of the soaps. They propose a procedure which eliminates the second transfer and simplifies the acidification of the soaps. This is accomplished by extracting the unsaponifiable material with ether in a Soxhlet extractor in the usual way and then replacing the boiling flask with one containing ether acidified with HCl. The HCl-ether complex is sufficiently volatile to distil into the extracting thimble where it completely acidifies the soaps, and the ether and HCl are readily evaporated from the acids collected.

In carrying out the Findley and Brown method a weighed sample (5 g) of carnauba wax was saponified by refluxing with 1 ml of 18.5*N* NaOH solution, 20 ml absolute ethanol, and 20 ml benzene for 20 hours. The solution was concentrated, transferred to an evaporating dish with hot benzene, evaporated, and dried completely in a vacuum desiccator. The dried residue was transferred as quantitatively as possible to a Soxhlet extractor thimble and unsaponifiable material was extracted with absolute ether for 100 hours. The solvent flask was then exchanged for one containing ether plus 2 ml concentrated HCl and extraction continued for 24 hours.

Hydroxyl and Acetyl Numbers. The various hydroxy compounds that occur in waxes form derivatives on heating with acetic anhydride, the acetyl radical (CH_3CO) replacing the hydrogen (H) of the hydroxyl (OH) groups. This serves the basis of analytical methods for the quantitative determina-

tion of these compounds. The *acetyl number* indicates the milligrams of potassium hydroxide required for the saponification of the acetyl group (CH_3CO) assimilated by one gram of wax on acetylation. On saponifying with alcoholic potassium hydroxide the acetyl is hydrolysed to acetic acid and combines with the alkali to form potassium acetate. The results are expressed in terms of milligrams to conform with the general practice in fat analysis.

The determination of acetyl number (or acetyl value) is the commonly accepted procedure for the estimation of hydroxylated esters, free alcohols (including sterols), and free hydroxy acids in an unhydrolysed wax. If the wax is saponified and the acetyl number is determined on the unsaponifiable material, it becomes a measure of the total amount of alcohols, free and combined, since the total amount of free and combined hydroxy acids will have been eliminated in the separation of the total acids fraction.

The procedure for acetylizing the wax, separating the acetylated wax, washing and drying same, and then taking an aliquot portion for the determination of the acetyl number as here given has been adapted from the method described by Lewkowitsch[14] for fats. Boil 10 grams of the wax with twice its weight of acetic anhydride in a round-bottomed flask under a reflux condenser for two hours; pour the resulting mixture into a large beaker containing 500 ml of hot water and boil for half an hour. Allow the mixture to separate into two layers, siphon off the water, and boil the oily layer with three successive portions of fresh water. All free acetic acid removed, the acetylated wax is carefully separated from water and further dried by filtering through anhydrous paper in a drying oven.

Weigh two grams of the acetylated wax and saponify with a measured volume of standard alcoholic potassium hydroxide as in the determination of the saponification number; evaporate nearly to dryness to expel the alcohol, dissolve the soap in water, and add an amount of standard sulfuric acid exactly equivalent to the alkali used for saponification. Warm gently until the fatty acids separate as a layer at the top. Filter through wet paper, wash with boiling water until filtrate is no longer acid, and titrate the filtrate and washings with tenth-normal alkali, using phenolphthalein as an indicator. Deduct the amount of alkali required to neutralize any soluble fatty acids in the original substance and calculate the acetic acid found in terms of acetyl number as defined above.

$$\text{Acetyl number} = \frac{\text{ml } N/10 \text{ KOH used to neutralize HA} \times 5.61}{\text{Wt. of acetylated product taken}}$$

The *hydroxyl number* of a wax is similar to the acetyl number, except that it corresponds to the acetyl value based on the original amount of wax taken instead of being based on the amount of acetylated wax; consequently

the hydroxyl number is a trifle higher than the acetyl number for most waxes.

There are several methods for the determination of the hydroxyl number of waxes. Benedikt and Ulzer (1887)[2] determined the acetyl number on the fatty acids after they were separated from the wax. Their method was based on the difference between the neutralization number and the saponification number of the acetylated acids; it was referred to as the acetyl ether number. Other methods are the Normann[23] method (1912), not widely used; the Elsbach method, described below; and the Meier[21] method (1951) also described below.

Elsbach Method. Two 5-g portions of the substance are weighed into a round-bottom flask with a side-inlet that reaches close to the bottom. A stream of carbon dioxide (CO_2) or nitrogen (N_2) is passed through while the flask is placed in an air bath at 100°C until constancy of weight is obtained. The flask contents are then acetylized with 4–6 ml of acetic anhydride under a reflux condenser for 1½ hours. After the substance is acetylized, dried CO_2 or N_2 is again blown through until excess of the acetic anhydride is drawn off, which takes 1½–3 hours, and the product is again weighed after displacing the CO_2, or N_2, by air. The gain in weight by acetylizing is represented by p in the following formula:

$$\text{Hydroxyl number} = p[56{,}104/42.036 \times 100] = 13.34p$$

$$\text{Acetyl number} = 13.34p/[1 + p/100].$$

As an example, analysis by the Elsbach method shows that white beeswax has a hydroxyl number of 15.0, and an acetyl number of 14.8.

Meier Method. 1–1.5 g of test material, 3 ml acetic anhydride, and 0.3 g anhydrous sodium sulfate are placed in a 100-ml Erlenmeyer flask with an air condenser connected through a ground-in glass joint. Some boiling chips are added. The material is refluxed for 2 hours over a small flame, allowed to cool, and is then taken up and transferred to a 100-ml separatory funnel with 50 ml petrolic ether. The bulk of the acetic anhydride is then shaken out and removed with water. The petrolic ether layer is washed with sodium bicarbonate solution and again with water until neutral to litmus, is dried over anhydrous sodium sulfate, is filtered back into the original flask, and is then evaporated to constant weight on the water bath and under reduced pressure. The flask containing the acetylated material is accurately weighed and its contents are saponified with 25 ml 0.5N alcoholic KOH for a half hour; the excess KOH is determined by titrating with 0.5N HCl and thymolphthalein or phenolphthalein. The saponification number of the acetylated material (V_{ac}) is calculated from the result (and a blank of the alcoholic KOH), and the saponification value of the original test material (V) is also determined. The hydroxyl number is calculated from ($V_{ac} - V$).

The amount of hydroxy compounds (H) can be estimated if the mean molecular weight (m) is known. In the Benedikt and Ulzer[2] and in the Lewkowitsch methods the formula is

$$H = \frac{c(m + 42.036)}{561.04d}$$

where H = amount (%), c = acetyl number, m = mean molecular weight, 42.036 is the constant for the mol. wt. of the acetyl group (CH_3CO) less the replaced H of the original OH group, and d is the number of hydroxyls.

A gravimetric method which measures the increase in weight of the fatty acids produced in acetylation employs the formula

$$H = \frac{im}{42.036d}$$

where i = increase in weight on acetylating.

Meier[21] reported the acetyl and hydroxyl numbers for alcohols and hydroxy acids as determined by the Meier method.

	Ac Number		OH Number	
	Found	Theory	Found	Theory
Octadecyl alcohol	180.6	180.5	208.9	208.8
Cetyl alcohol	197.5	195.7	231.8	229.5
Beeswax alcohols	121	—	133.1	—
Carnauba wax alcohols	105	—	114.0	—
Woolwax alcohols	160	—	181.8	—
Ricinoleic acid	164.9	164.8	188.2	188.8
Dihydroxystearic acid	280.3	280.1	354.9	354.6

Pyridene-Acetic Anhydride Method. Findley and Brown[7] contend that the determination by direct acetylation has not been successful with waxes because the mixed anhydrides formed by the reaction of free wax acids and acetic anhydride (A_2O) are difficult to hydrolyse quantitatively before titration. In the improved West pyridene-acetic anhydride procedure of Ogg and his co-workers (1945) the wax is completely precipitated by the water added to decompose the excess A_2O. Findley and Brown have improved the Ogg[24] method by the use of added water, for hydrolysis, in a pyridene solution. The reagents are a 10 per cent solution of dry distilled A_2O in dry distilled pyridene, and water-pyridene prepared by incorporating 10 per cent of water in pyridene. Details of the analytical procedure to obtain concentration of OH groups in moles per kilogram are given by the authors.

In their procedure the titration is corrected for the amount of free acid in the wax sample; the free acid must be determined separately. The calculations are based on the saponification numbers of the acetylated wax and of the original wax.

TABLE 85. HYDROXYL NUMBER ON ORIGINAL PRODUCT (MASS METHOD)

	Molecular Weight	Saponification Number	Theoretical Hydroxyl Number
Hydroxy Acids			
Ricinoleic, $C_{17}H_{32}OH \cdot COOH$	298.45	187.99	188.79
Dihydroxystearic, $C_{17}H_{33}(OH)_2 \cdot COOH$	316.47	177.28	354.56
Free Alcohols			
Cholesterol, $C_{27}H_{45}OH$	386.64	—	145.11
Sitosterol, $C_{29}H_{49}OH$	414.69	—	135.29

ACETYL GRAVIMETRIC PROCESS ON ORIGINAL PRODUCT

	Molecular Weight	Mol. Wt. After Acetylating	Theoretical Increase in Wt. (per gram)
Hydroxy Acids			
Ricinoleic	298.45	340.49	0.1409
Dihydroxystearic	316.47	400.55	0.2657
Free Alcohols			
Cholesterol	386.64	428.68	0.1087
Sitosterol	414.47	456.51	0.1013

ACETYL NUMBER ON ACETYLATED PRODUCT (BENEDIKT *et al.*)

	Molecular Weight	Saponification Number	Theoretical Acetyl Number
Acetylated Hydroxy Acids			
Ricinoleic, Ac.	340.49	329.56	164.78
Dihydroxystearic, Ac.	400.55	420.20	280.13
Acetylated Free Alcohols			
Cholesterol, Ac.	428.68	—	130.88
Sitosterol, Ac.	456.51	—	122.89

For an alcohol the difference between the saponification number of the material before and after acetylation ($V_{ac} - V$) becomes simply V_{ac} since $V = 0$.

For example, if V_{ac} for a sample of dotriacontanol were determined as 119, the concentration of OH (moles/kg) would be 119/56.1 = 2.11. Dotriacontanol ($C_{32}H_{66}O$) has a molecular weight of 466.858, hence its hydroxyl number is 56104/466.858 = 120.2. The concentration of OH (moles/kg) can be calculated as 120.2/56.1, or simply 1000/466.858.

In the gravimetric methods for determination of hydroxy compounds the following formula expresses the concentration of OH groups as moles per kilogram when the mean molecular weight and acetyl number have been analytically determined.

$$\text{Conc. OH (moles/kg)} = \frac{1000c(m + 42.036)}{m \times 56104\,d} = \frac{c(m + 42.036)}{m \times 56.104\,d}$$

where c = acetyl number, m = mean molecular weight, and d = number of hydroxyls.

In testing the improved pyridene-acetic anhydride method, Findley and Brown[7] obtained OH values (mole/kg) for carnauba wax alcohols, dotriacontanol, dihydroxystearic acid, and behenic acid of 2.41, 21.3, 6.24, and 0.07 respectively, compared with 2.44, 214, 6.32, and 0.00 for theoretical values.

Acetylation of Alcohols. Findley and Brown[7] acetylated carnauba wax alcohols by boiling the alcohols with twice their weight of acetic anhydride for 6 hours, and removed excess anhydride under a vacuum at 100°C, finally at 1 mm pressure. Subsequent washing of a sample of the acetates with hot water did not lower the saponification number appreciably. From 91.5 g of alcohols they obtained 100.3 g of acetates having a mean saponification number of 119.9. Saponification values were taken on individual acetylated alcohols obtained in the fractionation of the mixed acetylated alcohols by molecular distillation at 0.50 mm pressure. These investigators followed the technique of "amplified distillation" in which hydrocarbon oils (commercial oil b. $pt._{0.5\ mm}$ 190–280°C and ceresin wax) are added to the acetylated alcohols before distillation. For details of procedure see Findley and Brown's paper[7].

Hydrogen Method of Determination of Alcohols. Since the wax alcohols can be converted into wax acids by means of soda lime in the following manner,

$$\underset{\textit{Cetyl alcohol}}{C_{16}H_{33}\cdot OH} + NaOH = \underset{\textit{Sodium palmisate}}{C_{16}H_{31}O_2Na} + 2H_2$$

it is possible to measure the amount of hydrogen involved, and on the basis of the volume of liberated gas to compute the amount of alcohol originally present. Lewkowitsch[14] gives the yields of 1 g of cetyl, ceryl, and melissyl alcohols as 184.4, 116.9 and 101.9 ml respectively at 760 mm pressure and 0°C temperature. These figures are equivalent to 1.652, 1.047, and 0.913 per cent respectively. (Theoretical: 1.663, 1.054, and 0.919.) The apparatus involved and details of manipulation are fully described by Lewkowitsch. The reader is also referred to modifications of the method therein described.

Hydrocarbon Analysis. In the determination of hydrocarbons in a wax, a separation from the alcohols of the nonsaponifiable can be effected by two well-known methods. The method of Leys depends upon treating the mixture with a hot amyl alcoholic solution of fuming hydrochloric acid (HCl) to dissolve the alcohols, whereas the hydrocarbons (HX) separate out as an insoluble mass. In the Lewkowitsch method the alcohols are converted to the corresponding acids by heating the sample with soda-lime or potassa-lime; cholesterol, if present, remains practically unchanged.

Leys[15] saponifies 10 g of the substance with 25 ml of alcoholic KOH (45 g of KOH in 1000 ml of absolute alcohol and 50 ml of benzene). Use is made of an apparatus which consists of

the top left and a stopcock fixture protruding from the middle of the flask at the right, which in effect is a combined saponification vessel and separatory funnel. When the saponification is completed, 50 ml of hot water are added and boiling is continued under a reflux condenser for a few minutes. The soap solution is drawn off while hot, and the benzene solution is evaporated to dryness in a porcelain dish. The residue is then transferred with 100 ml of hot amyl alcohol to a beaker, and an equal volume of fuming HCl is added. This is then boiled over an asbestos plate; the alcohols dissolve, whereas the hydrocarbons are taken off and boiled out once more with a mixture of 25 ml amyl alcohol and 25 ml fuming HCl. After cooling, the cake of HX is taken off and rinsed with water, the acid solution is drawn off, and the amyl alcohol solution is well washed. The amyl alcohol is finally distilled off and the residue dissolved in benzene. After evaporation of the benzene, the residue is weighed. The alcohols may be further examined if so desired.

If the hydroxyl number is determined on the unsaponifiable portion of the wax and the mean molecular weight of the alcohols derived through acetylation is taken, the amount of alcohols can be computed and deducted from that of the unsaponifiables to obtain the amount of hydrocarbons. Or, if the hydroxyl number is determined on the unsaponifiables and the mean molecular weight of the unsaponifiables is determined, through functional group analysis[7], the amount of hydrocarbons can be calculated from the molar concentrations, as in the following example. The mean molecular weight of the unsaponifiables of commercial carnauba wax was found to be 336, equivalent to 1000/336, or 2.73 mols/kilo[7]. The hydroxyl number was analytically determined as 136.4, or an OH concentration of 561.04/136.4, or 2.43 mols/kilo. Therefore the hydrocarbons amount to $2.73 - 2.43 = 0.30$ mol/kilo. Since the wax contained 51 per cent of unsaponifiables, the amount of hydrocarbons would have a concentration of 0.31×0.51, or 0.15 mol/kilo. Since all plant waxes have $C_{31}H_{64}$ (mol. wt. 436.8) as the chief hydrocarbon constituent, the hydrocarbons would amount to $436.82 \times .15 \times 100/1000 = 6.5$ per cent.

In instances where the hydrocarbons have been isolated from the unsaponifiables by the "hot amyl alcohol-fuming HCl treatment" an ultimate analysis readily gives the C to H ratio (roughly $C_{30}H_{62}$ for carnauba wax), leading to a calculated amount of 6.3 per cent.

Sterol Analysis. Digitonin, a glucoside of digitalis leaves, is the reagent depended upon to precipitate sterols such as cholesterol and others. If a hot solution of 1 g of digitonin in 100 ml of 90 per cent ethanol is added to a solution of cholesterol in ethanol, a substance known as digitonin-cholesteride is precipitated in crystalline form. After standing an hour it is filtered, washed, and dried at 110°C. The crystals are soluble in pyridene, but insolu-

ble in water and in most solvents; they are very slightly soluble in methanol and less soluble in hot ethanol. Phytosterols, stigmasterol, and many alcohols of other series form similar digitonides, but the esters of the cholesterols do not interact with digitonin.

Test: 50 g of sample are shaken hot in a separatory funnel with 20 ml of 1 per cent solution of digitonin (in 96 per cent alcohol) for 15 minutes. After standing several hours the lower layer is drawn off and 50–100 ml ether are added. After shaking, the solution is filtered. The air-dried digitonide is ground, and extracted with ether when it is heated with 2 ml acetic anhydride for ½ hour. When cool the acetates separate.

Phytosterol acetate separates white while the cholesterol is brown. After two crystallizations from alcohol the melting point of the acetates is determined.

Microtechnique for the determination of phytosterols in leaf meals has been worked out by Wall and Kelly[27] of the U. S. Department Agriculture, Philadelphia, Pa. In the microprocedures the petrolic ether extract containing the sterols was purified by passing through a Super-Cel and activated magnesia adsorption column and treated with iodine to remove carotene. The sterols are then precipitated with digitonin and estimated colorimetrically by the Libermann-Burchard reaction with the sterol digitonides. This reaction is one in which the sterol is dissolved in chloroform and treated with acetic anhydride and sulfuric acid.

In the macromethod the sterols are purified similarly, but carotene is not removed except in colorimetric samples. The petrolic ether is evaporated; the sterols are dissolved in alcohol and precipitated with digitonin as digitonides, and the precipitate is weighed. The precision of these methods is 5± per cent. If the steroids are in combined form they are hydrolysed with alkali and treated as above. Saturated sterols can be separated from unsaturated by treatment with acetic anhydride and concentrated sulfuric acid in chloroform, and estimated gravimetrically.

In the *Liebermann-Burchard reaction* with the digitonides, two types of transmission curves can be found, one with a broad absorption band between 620 and 680 mμ, and one with a sharp absorption band at 680 mμ. Spinasterol and the sterols of alfalfa, beet, spinach, etc. show the latter. β-Sitosterol and the sterols of cabbage, carrot, corn, etc. show the broad absorption band. The sterols of most leaves are unsaturated. Where saturated sterols occur they constitute 50 per cent or more of the total sterols. Only a small proportion of the sterols are in combined form.

Luddy, Turner, and Scanlan[18] have successfully applied the spectrophtometric determination of cholesterol and triterpene alcohols in the case of woolwax. The determination of cholesterol is made at 630 mμ and that of triterpene alcohols at 550 mμ. The absorptivities of the Liebermann-Burchard color complexes are computed from the formula

$$\text{Absorptivity, } a = \frac{\text{absorbance}}{cl}$$

where c = total conc. g/liter, and t = layer thickness in cm. Average a values for cholesterol were 5.00 and 1.50 for 630 and 550 mμ respectively, designated as a_C and $a_{C'}$. Average values for lanosterol were 5.50 and 0.46 for 550 and 630 m respectively, and designated as a_L and $a_{L'}$; and 4.79 as the a_{CD} value of cholesterol digitonide at 630 mμ. The equations which determine the cholesterol and triterpene alcohols in the free alcohols of wool-wax are

$$\text{Cholesterol, wt. \%} = \frac{100(a_{630}a_L - a_{550}a_{L'})}{a_Ca_L - a_{C'}a_{L'}}$$

$$\text{Triterpene alcohols, wt. \%} = \frac{100(a_{550}a_C - a_{630}a_{C'})}{a_Ca_L - a_{C'}a_{L'}}$$

In the calculation of the percentage by weight of cholesterol in esters, the denominator of the first formula is multiplied by 1.2; the one for triterpene alcohols remains unchanged.

The amount of cholesterol in cholesterol digitonide is given by the formula

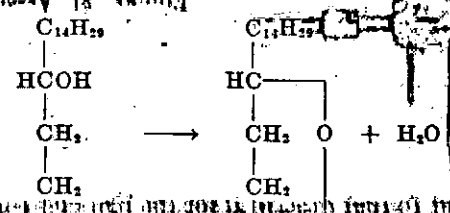
$$\text{Cholesterol, wt. \%} = \frac{a_{630}}{a_{CD}}\,100$$

The analytical procedures of three methods have been given in detail by Findley and Brown[7].

Sterols can be separated from each other by the method of Windaus and Hauth[29], that is, by brominating the acetic ester in a mixture of glacial acetic acid and ethyl ether. It is possible, for example, to separate *stigmasterol* as an insoluble tetrabromostigmasterol acetate from the soluble dibromo *sitosterol* acetates. After purification, tetrabromo derivative cannot be very well distinguished by its melting point because it is not definite, but the derivative can be debrominated and the melting point determined on the acetate. Stigmasterol acetate has a melting point of 139°C, and a specific rotation of −51°. The conversion of the acetate to stigmasterol to the tetrabromo derivative is not quantitative but amounts to about 70 per cent.

Qualitative Check Tests for Sterols. One of the useful tests for sterols is the *Salkowski reaction*, in which a solution of the specimen in chloroform is shaken with concentrated sulfuric acid. If positive, the colors appear in both layers. In the *Lifschütz reaction* the specimen together with a small amount of perbenzoic acid is heated in glacial acetic acid, and sulfuric acid is added to the solution. In the *Rosenheim reaction* the substance to be tested is dissolved in chloroform and a few drop of an aqueous solution of trichloracetic acid are added. In the *Tschugajeff reaction* the specimen is dissolved in glacial acetic acid, then treated with zinc chloride and acetyl chloride, and boiled to secure the color reaction.

Lactone Number. A serious difficulty, which often confronts the chemist in the analysis of fatty acid mixtures, is the unstable character of the hydroxy-fatty acids. The latter are either lactone-forming or nonlactone-forming. Lactone-forming hydroxy acids (more especially the γ acids) show a pronounced tendency to form inner anhydrides after being liberated. Thus γ-hydroxystearic acid, after separation from its salts or esters, passes immediately into stearo-lactone:



Hydroxystearic acid → *Stearo-lactone*

The nonlactone-forming hydroxy acids do not possess the property of yielding inner anhydrides. The hydroxyl group is therefore free to react with acetic anhydride during acetylation.

Hydroxystearic acid, $C_{17}H_{34}OH \cdot COOH$, of molecular weight 300.468, requires for saponification 1 molecular equivalent weight of KOH, 56.104. The milligrams of KOH necessary to neutralize and saponify 1 gram of hydroxystearic acid are then $56{,}104 \div 300.468 = 186.72$, the acid and saponification number. However, if the lactone exists with the hydroxy acid, the acid number will come way down, and the saponification number will be a trifle higher than if no lactone were present. For this reason an ether number will be shown that would otherwise be zero. This gives us an estimation of the amount of lactone.

	Acid Number	Saponification Number	Ether Number
Hydroxystearic	186.85	186.85	0
Hydroxystearic and stearolactone 1:1	96.31	192.62	96.31

The mean molecular weights of the lactone acids are calculated from the formula

$$m = \frac{56{,}104}{S - 18.016(S - a)},$$

where m = mean molecular weight, S = saponification number of mixed fatty acids, and a = acid number.

The lactone number is defined as the mg of KOH necessary to saponify

the lactone in 1 g of acids. The lactone number is lower in the acetylated mixture.

	Acid Number	Sapn. Number	Ether Number	Acetyl Number	Lactone Number
Nonacetylated	96.31	192.62	96.31	—	96.31
Acetylated	89.83	269.50	179.67	89.83	89.83

Hübl Number. The Hübl number is the ratio of the saponification number of the neutral portion (wax esters, alcohol, and hydrocarbons) to the acid value. In general the ratio number is the ester value divided by the acid value for a natural wax, and amounts to 3.6–3.8 for genuine beeswax, for which it is commonly used to detect adulteration with East Indian waxes.

Reichert-Meissl Number. The Reichert-Meissl (R-M) number may be defined as the number of milliliters of tenth-normal (0.1*N*) alkali required to titrate the acids obtained by distilling 5 grams of oil, fat, or wax.

Butyric (C_4), caproic (C_6) and to some extent caprylic (C_8) acids are classed as the volatile fatty acids readily or slightly (C_8) soluble in water which are included in the R-M figure. On the other hand, caprylic (C_8), capric (C_{10}), lauric (C_{12}), and also myristic (C_{14}) acids belong in the category of volatile fatty acids which are almost incompletely soluble in water (C_8 excepted) and which are the basis of the value referred to as the *Polenske number*.

The R-M value of butter usually ranges between 24 and 34, coconut oil from 6 to 8, and palm oil from 0.9 to 1.9; but for most oils, fats, and waxes the R-M number is less than 1.

Polenske Number. The *Polenske number* may be defined as the number of milliliters of tenth-normal (0.1*N*) alkali required to neutralize (by titration) the insoluble volatile fatty acid distilled from 5 grams of oil, fat, or wax. Caprylic (C_8), capric (C_{10}), lauric (C_{12}), and myristic (C_{14}) acids come in this category.

Coconut oil gives Polenske values of 16.8–17.8, palm oil 8.5–11.0 and, butter fats 1.5–3, but for true waxes the value approaches 0, and for those vegetable tallows that are classed as waxes the Polenske number is less than 2.

Carbonyl Group or Ketone Determination. Findley and Brown[7] have described a method of determining the carbonyl (CO) group. The wax sample is dissolved in toluene and reacted with hydroxylamine hydrochloride to form an oxime and hydrochloric acid. The acid liberated is titrated directly with alcoholic alkali. Hydroxylamine hydrochloride reagent, *N*/2, is prepared by dissolving $NH_2OH \cdot HCl$ in absolute ethanol and neutralizing with alcoholic alkali to thymol blue just before use. Analytical procedure details have been described by these authors. Aldehydes interfere with de-

termination of CO since they react with the reagent in the same manner as ketones.

DETERMINATIONS OF PHYSICAL CONSTANTS

The physical constants that are given consideration in the analyses of waxes are: (1) color, odor, and taste; (2) melting, setting, and solidification points; (3) specific gravity or density; (4) hardness and needle penetration; (5) percentage contraction through temperature range from above to below the solidification point; (6) refractive index; (7) plastic point or blocking temperature; (8) tensile strength (largely for paraffines or coating waxes); (9) viscosity of the melts; (10) ductility, flexibility, and modulus of rupture (mostly for hydrocarbon waxes); (11) flash and fire points; (12) oil content (hydrocarbon waxes); (13) electrical constants; (14) solubility in polar and nonpolar solvents.

Color, Odor, and Taste. The color of a wax may be white, straw, pale amber, tan, brown, etc. In the melted state, the color of paraffin waxes is determined by means of a Saybolt Chronometer according to standard ASTM method D 156-38. Special heating coils to maintain the wax in liquid state must be used while the color is being read. By the use of this apparatus the color of the column of melted wax is matched with the color of standard glass color discs, the exact match being obtained by varying the depth of the column as required. Colors determined by this method are expressed as values ranging from −16 to +30. The scale is such that the higher positive values denote the lightest colors; for example, fully refined paraffin waxes have values from +18 to +30.

Aside from the *Saybolt color method*, colors of waxes are sometimes expressed in the terms of the *Lovibond scale*, or by the *NPA color standard*. These latter methods require matching the color with a colored slide. The Saybolt method employs discs of gray-colored glass, and is limited to the white and off-white waxes.

The NPA (National Petroleum Association) scale ranges from ½ (palest) to 8 (darkest) in amber colors. Since the very dark microcrystalline waxes rate darker than 8, the specimen of wax is diluted (15% stock by volume with 85% water white kerosene) for rating, in which for example a trifle darker wax than 8 might then rate 3. If the wax specimen still is too dark for rating, the test is continued using a double dilution. It is to be noted that the system of rating is the reverse of the Saybolt color standard. Melted specimens of wax are measured for color in all three procedures, except when it becomes necessary to dilute very dark waxes in order to arrive at their color.

The odors of some of the natural waxes are somewhat pronounced, such as the odor of beeswax, and the odor of carnauba wax. They are even more

pronounced when the waxes are melted. Such odors are not objected to as they are characteristically pleasant, at least for the waxes of high quality. On the other hand, the odor of residual solvent in a microcrystalline wax if present, might preclude its use for coating paper, etc. In determining the odor the specimen of wax is melted in a small dish made of aluminum foil, and compared with a similar melt of approved standard. The difference in odor of the test and blank specimens is then recorded.

There are occasions now and then when it becomes necessary to taste a wax. Refined waxes are ordinarily free from taste. A few waxes have a distinctive or characteristic taste of a mild degree, and the nature of the taste is then recorded.

Melting and Setting Points. The melting point of a wax and of its constituents is in general valuable not only in identifying and classifying the wax, but in establishing its purity.

The setting point, which is the temperature at which the molten wax begins to set for solidification, is substantially the same as the melting point for pure chemical compounds, but often widely different from the melting point for mixtures of compounds.

Setting and melting points are determined by (a) closed capillary tube, (b) open capillary tube,(c) thermometer bulb method (drop point).

The melting point by method (a) or (b) is usually determined with a simple apparatus, consisting of a 100-ml beaker two-thirds full of a liquid of a high boiling point; a ring stand with clamps to hold a thermometer; a stirrer, e.g., a glass rod with a ring ¾ inch in diameter bent at right angles to the rod; a thermometer graduated by tenths of a degree; and several capillary tubes.

Drop Point Method. The dropping or drop point method requires that the thermometer with the wax applied to its bulb be inserted through a stopper into air or a gaseous zone, usually in a Pyrex test tube. The liquid in the beaker surrounding the test tube is selected from one of the following: water, sulfuric acid, olive oil, glycerin, phosphoric acid, or paraffin. However, jojoba oil if available makes the best heating medium.

Open Capillary Tube Method. The end of a piece of quill glass tubing is drawn out into a capillary. The substance is melted at a temperature slightly above the fusing point and then drawn up into the capillary tube, where it is allowed to solidify spontaneously. After an interval of not less than one hour and preferably twelve hours the tube, open at both ends, is attached by a cork or an elastic band to the stem of a thermometer in such a manner that the substance is at the same level as the bulb. The thermometer with its tube is then immersed in water, which is gradually heated at a rate not exceeding 0.5°C per minute until fusion of the contents of the capillary takes place, when the temperature is recorded. It is desirable to immerse the

beaker of water containing the thermometer in an outer vessel also filled with water, and to apply the source of heat to the latter.

Closed Capillary Tube Method. A modification of the above described method is the use of a capillary tube about 2 inches long; the end is sealed off and the fragments of wax are placed in the capillary, or the capillary is flamed and the melted wax drawn in as the capillary cools. The thermometer with the capillary strapped to it is placed in the inner tube of a Fisher apparatus, which consists of an outer and inner glass tube, the latter with perforations and corks. When heat is applied to the outer tube by a microburner, the perforations on the inner tube set up convection currents in the liquid medium used, thereby producing a uniform temperature, necessary for exact determination of the melting point.

U-Tube Melting Point. This determination is done in the same manner as above, except that a U-tube capillary is used instead of a straight capillary. The melted wax is inserted in a U-tube which has a long and short leg, and the wax is then congealed. In the determination, at the critical moment the wax in the long leg will melt, and drop to the level of the rising wax in the short leg.

ASTM Methods. In the standard test method for the melting point of paraffin wax as adopted by the American Society for Testing Materials, the melting point is defined as the temperature at which melted paraffin wax, when allowed to cool under definite prescribed conditions, first shows a minimum rate of change. It also notes that the so-called "American melting point" is an arbitrary figure 3°F higher than the ASTM melting point. The ASTM determination is really one of a setting point. For details of the method and the construction of the melting point apparatus the reader is referred to ASTM designation D 87-42, revised 1942. The apparatus consists of a wax container, air bath, water bath, stirrer, test tube, thermometer, and bath thermometer. "The melting point thermometer reading, estimated to 0.1°F, shall be observed and recorded every 15 seconds for at least 3 minutes after the temperature again begins to fall after remaining almost constant. The record of temperature readings shall then be inspected and the average of the first five readings that lie within a range of 0.2°F shall be considered as the uncorrected melting point. The temperature shall be corrected for error in the thermometer scale."

In the ASTM Method of Test for the Melting Point of *Petrolatum*, the melting point is defined as the temperature at which petrolatum becomes sufficiently fluid to drop from the thermometer used in making the determination under definite described conditions. This is essentially the drop point method. In preparing the specimen the "thermometer bulb is chilled to 40°F, wiped dry, and while still cold thrust into the melted petrolatum so that approximately the lower half is submerged. It shall be withdrawn

immediately, held vertically away from the heat until the surface dulls, and then placed for 5 minutes in a water bath having a temperature not over 60°F."

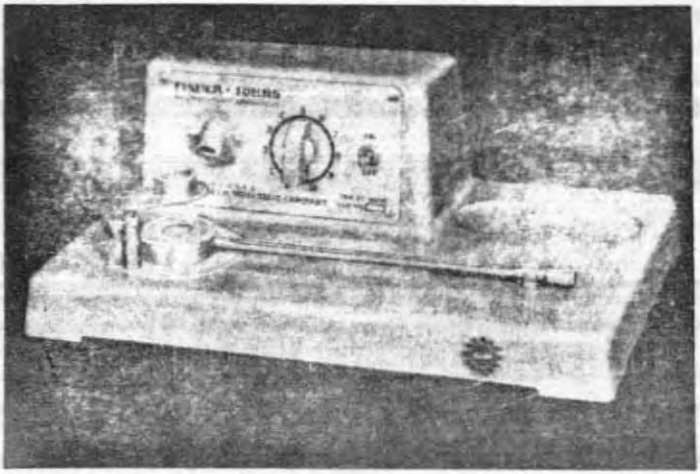
Dewar Flask Method. The specimen is put in a Dewar flask and heated on a water bath to some 5 degrees above its melting point. The bulb is taken from the water bath and constantly shaken and as soon as a skin begins to form the thermometer is read every minute and the cooling point plotted. The knee of the curve shows the melting point.

The above method is essentially the freezing point method of Zhukov modified by Kissling[10]. In the Zhukov method 35 ml of paraffin wax are kept about 10 degrees above its freezing point for 30 minutes in a 50-ml Dewar flask provided with a thermometer graduated in 0.1 degrees then allowed to cool and the temperature read at minute intervals after the liquid becomes cloudy until it remains constant for several minutes. Kissling place the flask in water, the water level being 1 cm above the paraffin. After heating for 30 minutes about 6 degrees above the freezing point the paraffin is stirred with a warm thermometer, which touches the bottom of the flask. The freezing point is the temperature at which a deposit of solid paraffin appears at the bottom of the flask.

Maquenne Melting Point Block. An electrical microapparatus for the determination of melting points consists of a cylindrical aluminum block in the bottom of which is a spiral hole. This spiral cavity contains the heating element, which is protected by aluminum oxide. The bulb of a thermometer lies horizontally in a hole bored near the surface of the block. The whole block is surrounded by a bronze ring which projects 4 mm above the surface of the block. The substance being tested is placed on a cover glass resting on the bronze ring. The melting of the sample (about 0.1 mg) is observed by means of a lens, after which the used sample is removed by a wad of filter paper.

Fisher-Johns Melting Point Apparatus. The Fisher-Johns apparatus, basically an adaptation of the Maquenne electrical microapparatus, was first produced by the Fisher Development Laboratories in 1937. The improved design has a powerstat control unit, and an illuminated heating-stage for measurements. A minute specimen of wax is placed between two small cover-glasses. This tiny "sandwich" is then placed in the circular depression on the heating-stage, and the heating rate set with a knob on the control face. A meniscus magnifier makes it possible to see the actual points at which the wax (a) starts to soften, (b) to spread, and (c) to fully melt. The side armored thermometer is graduated from 20 to 300°C. The apparatus is available for use on 115 volt 60 cycle a.c. circuit.

Ubbelohde Drop Point. The Ubbelohde drop point apparatus consists of a porcelain scale thermometer (range 0–110° in 1/1°C) to which a cylindrical metal sleeve is attached, a metal case which screws onto the metal sleeve with



Courtesy Fisher Scientific Co., Pittsburgh, Pa.
FIGURE 20. Fisher-Johns melting point apparatus.

a small opening that acts as a pressure equalizer, and a cylindrical glass cup opening at the bottom 3 mm in diameter. The apparatus was designed primarily for determining the melting point of greases, but it may also be used for soft waxes. The procedure is to fill the glass cup with the sample of wax and then fit it in the metal case that is in pressure contact with the thermometer bulb. When the wax melts it will always form a drop close to the size of the 3-mm aperture.

Softening Point. The softening point of a wax is the temperature at which the solid wax begins to soften. A wax will soften more readily when heated in contact with water than when perfectly dry. The softening point will also vary to some extent with the weight applied to the test specimen. Since in technical use waxed surfaces frequently come in contact with liquids under pressure it becomes necessary to recognize the temperature at which the wax will lose its firmness and perhaps its utility as well.

Ring-and-Ball Method. Although the ring-and-ball method (ASTM designation E 28-42 T, revised 1942) is one which was designed as a test for asphalts, tars, pitches, and resins, it is of considerable value in determining the softening point of many types of waxes. The apparatus is equipped with one, two, or four rings to use with the same number of balls. An equipment with single ring is shown in Figure 21.

The procedure is to prepare carefully a sample of melted wax and to pour it into the ring or rings which rest on a brass plate. After the wax has congealed the excess on the surface is cut off clean with a slightly heated spatula. The glass container is then filled with 9 cm of water, or with glycerol if the wax melts above 80°C. The ball is centered on the upper surface of the

sample. The ring containing the sample should be suspended in the water so that the lower surface of the filled ring is 2.5 cm above the bottom of the glass container. The thermometer is suspended so that the bottom of the bulk is level with the bottom of the ring. The ball is finally placed in the center of the upper surface of the material in the ring.

The heat is applied to the container in such a manner that the temperature of the bath is raised 5 degress each minute. The temperature reading indicated by the thermometer at the instant the sample touches the bottom of the container is taken as the softening point. The reader is referred to the "Tentative Method for Test for Softening Point, Ball and Shouldered Ring Apparatus," published by the American Society for Testing Materials, for a more detailed description, and for designs of apparatus with multiple rings.

Ring-and-Plunger Method. Instead of the ring-and-ball method the softening point may be determined by a ring-and-plunger method. In the latter method the steel ball is replaced by a brass plunger, which is guided by a brass wire framework with rings at both ends.

The plunger has a shank 9.52 mm in diameter and 95 mm long. It is flanged to 20 mm at top end, and 17 mm at base end to which there is a pointed tip. The tip is 7.9 mm deep, and of large radius tapering from 3.2 mm to a dull point. The total weight of the plunger is 75 grams. The frame is 178 mm high with support ring 31.7 o.d., 25.4 i.d., 12.7 mm deep, and has a lower ring 15.9 o.d., 12.7 i.d., 6.35 mm deep, for holding the wax specimen (See Figure 22).

The procedure in making the ring-and-plunger softening point determination is quite similar to that described for the ball-and-ring method. The ap-

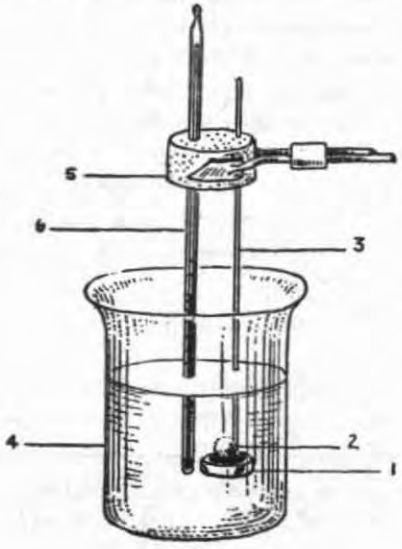


FIGURE 21. Assembly of ball and shouldered ring apparatus, showing single-shouldered ring. (1) brass-shouldered ring; (2) steel ball, 9.53 mm in diameter, weighing 3.5 grams; (3) brass wire support for ring; (4) 600-ml low-form Griffin beaker; (5) rubber or cork stopper; (6) thermometer.

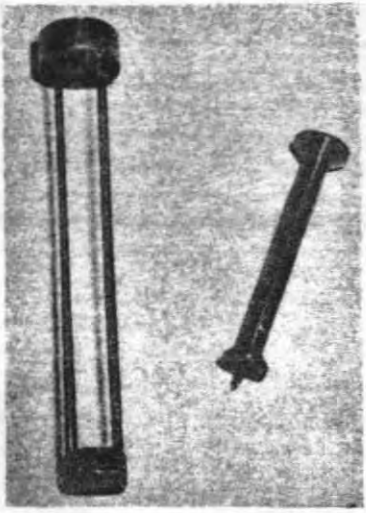
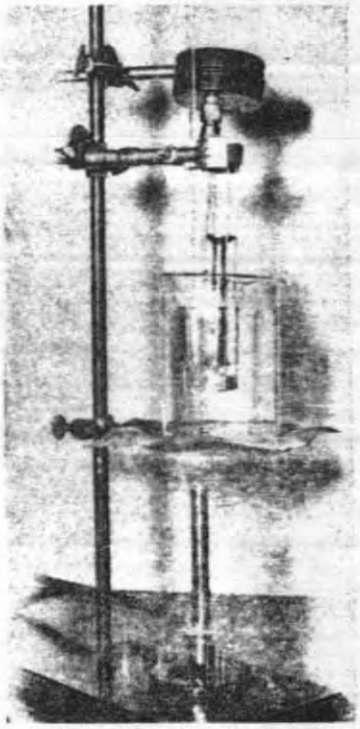


FIGURE 22. Ring and plunger for softening point determinations. *left:* Frame with ring filled with wax. *right:* Plunger.



Courtesy Crown Cork and Seal Co., Baltimore, Md.

FIGURE 22a. Assembly of apparatus showing position of frame and plunger for operation, electric stirrer, and thermometer.

paratus assembly is shown in Figure 22a. When the wax specimen softens in the ring under heat the tip penetrates deeply and the base of the plunger touches the ring which holds the specimen. The temperature at that instant is noted as the softening point of the wax.

Solidification Point. This determination is made under the following conditions:

(1) The temperature of the water bath at the start of the experiment should be the same as that of the wax in the test tube.

(2) The mixer in the water bath should remain in motion throughout the period of test.

(3) The temperatures used at the start of the experiment should be 5°F above the drop point of the wax.

(4) When clouding occurs in the test tube, the temperature of the water bath should be recorded. This will give the first indication of the solidification point.

(5) When clouding occurs in the test tube, the temperature of the wax should be recorded, and the stop-watch set in motion. The temperature should be taken after every half minute. The temperature, which has remained constant for a half minute, is the solidification point.

The temperature of the water bath when clouding of the wax first occurs, and the temperature of the wax which has remained constant for a half-minute, will not vary more than 0.5°F. The latter temperature should naturally be a trifle higher than the former. The great advantage of this method is that the clouding of the wax is uniform over the entire inner wall of the test tube.

Continental Solid Point Method. In this method, known as the Galician method, the bulb of a standard 1°F division thermometer is dipped into molten wax at about 20°F above its melting point. By holding the thermometer in the hands at an angle of about 15 degrees above the horizontal, a drop of molten wax will be formed on the lower end of the bulb. The thermometer is then slowly rotated on its axis and a reading of the temperature is taken at the point at which the drop solidifies and rolls to the top of the thermometer[20].

U. S. Army Ordnance Method [AXS-1015, 6-24-43]. In this method, which is a modification of the open capillary method, a capillary tube 4 mm in diameter and 7.25 cm (3 in.) long is filled on one end to a depth of 1.25 cm (0.5 in.) with a wax plug. After the wax solidifies the tube is fastened to the bulb of a thermometer and immersed to within 0.6 cm (¼ in.) of the top in a water (or mercury) bath, the temperature of which is raised at 3°F per minute until the wax plug rises as a result of the hydrostatic pressure. This point is called the melting point[20].

Melting Points of Petroleum Waxes. Marshall[20] stated that there are three points near the transition point from solid to liquid wax. The first is the *thaw point** or the eutectic temperature of the wax, and this is approximated by the ring and plunger method. The second is the *melt point* or the point at which all wax is actually liquid, and is best evaluated by the ASTM paraffin melting point (D 87-42) for all waxes. The third is the *flow point* or the point at which the viscosity is reduced to about 50 centistokes, and is best evaluated by the ASTM petrolatum melting point (D 127-130) method. High melting, hard microcrystalline waxes are subject to viscosity hysterisis at the melting point, but other petroleum waxes are not. Marshall has made a comparison of the results obtained by applying nine melting point methods to samples of waxes of four different types, as is shown in Table 86.

* Term for multi-component system—"Textbook of Physical Chemistry," S. Glasstone (1940) p. 739 *et seq.*

TABLE 86. A COMPARISON OF MELTING POINT METHODS (MARSHALL[20])

	Method Number*								
	1	2	3	4	5	6	7	8	9
128 AMP Paraffin	57.0	56.0	55.4	59.0	—	—	56.0	54.5	56.9
Plastic microcrystalline waxes	63.3	62.2	61.3	63.7	—	57.7	63.0	59.6	61.8
	75.0	74.2	73.4	78.2	66.3	62.6	73.9	74.5	73.9
	76.7	76.0	76.0	76.7	—	71.8	76.7	72.8	71.7
Oxidized hydrocarbon waxes	83.5	80.2	80.0	82.1	65.0	66.1	82.7	79.4	81.6
	83.8	83.8	80.0	86.1	75.0	69.8	82.6	80.6	82.7
	87.6	85.0	84.5	84.4	81.2	67.8	85.0	82.8	81.6
Hard high melting microcrystalline waxes	87.6	87.0	83.8	90.2	81.5	78.3	85.7	85.0	84.4
	88.4	87.8	85.5	90.2	85.0	81.2	95.8	86.4	87.5
	92.7	88.8	86.0	92.8	81.0	77.1	96.6	85.6	87.8
	93.8	90.3	86.0	95.5	87.0	83.5	97.0	85.0	86.0

* Method of application:

(1) A.S.T.M. Petrolatum Melting Point (D 127–130)
(2) A.S.T.M. Paraffin Melting Point (D 87–42)
(3) Continental Softening Point (Galicium)
(4) Ring and Ball Softening Point (ASTM D 28-427)
(5) Fisher Melting Point Block
(6) Crown Cork & Seal Ring and Plunger
(7) Solidification Point (Wurth)
(8) Ordnance Melting Point (AXS-1015)
(9) Capillary Tube Melting Point

Density. The density (absolute density), d, of a substance, such as wax, is the mass divided by its volume, $d = \frac{m}{v}$, referable to the temperature (t) at which the density is considered. For example, d_{15}, or d^{15}, means that the volume of a certain weight of the substance was measured at 15°C. Since in the cgs system the density of a unit volume of water is 1.0000 at 4°C, the expression d_{15} is derived from the ratio $dm_{t_{15}}/dv_{t_4}$ with unity as the denominator. The use of the expression d_4^{15} would be superfluous, that is, the simple expression d^{15} is to be preferred and the one to use.

Specific gravity (sp. gr.) is an expression of relative density of a substance to that of water. For example, the specific gravity may be recorded as: sp. gr. t_2/t_1, where t_2 is the temperature of the substance, and t_1 the temperature of the water. Specific gravity determinations are frequently made at 15, 20, and 25°C. and the densities compared with water at 15°C, whence the specific gravites are recorded as sp. gr. 15°/15°, 20°/15°, 25°/15°C, or as sp. gr. (d_{15}^{15}), (d_{15}^{20}), or (d_{15}^{25}) without using the temperature scale symbol.

To convert sp. gr. (d_{15}^{25}) to sp. gr. (d_4^{25}), that is, d_{25}, it is necessary to multiply by the density of water at 15°C, namely by 0.999173. For example, the specific gravity of stearic acid at 80°/15°C was 0.837; its density (d_{80}) would be 0.8397 × 0.999173, or 0.8390. The specific gravity 80°/4°C 0.8390 is the same as d_{80} 0.8390, or d^{80} 0.8390. It can also be written as sp. gr. (d^{80}) 0.8390.

Specific Gravity Determinations. The specific gravity of a wax is usually determined at a temperature close to room temperature, and at or somewhat above the temperature of its melt. A determination of the specific gravity can be conveniently made at 98–100°C for most waxes.

The specimen of wax should be melted and then slowly cooled, when it is allowed to remain for a number of hours at a temperature somewhat below that at which the determination is to be made. A customary procedure is that of following the Archimedes' Principle, namely, to weigh the specimen in air and in a liquid, customarily water, and to determine the density by the difference in weight. Let the volume of the solid be v, its density d; then the mass (m) is dv, and its weight dvg. When it is totally immersed in a liquid the volume of the liquid displaced is also v, and if its density is d', its weight is $d'vg$. This is the force upward, if the solid does not rest on the bottom of the vessel. The difference in the two weighings, $dvg - d'vg$, may be expressed by the equation $mg - m_1g = vd'g$. Writing $v = m/d$ in this equation and solving for d, we have $d = \frac{M}{m - m_1}$, that is, the numerical value for the density will be found by dividing the weight in air (strictly in vacuum for absolute density) by the loss in weight of water.

If a solid has a density less than that of the liquid, which is the case with

most waxes, it may be immersed in the liquid by hanging some very heavy solid below it and then keepting the last solid immersed in the liquid during both weighings. Let m_2 be the apparent mass of the sinker when weighed in the fluid, and M the apparent mass of both sinker and specimen in the fluid; then as the loss of weight is proportional to $m + m_2 - M$, the density is given by $d = \frac{m}{m + m_2 - M} d'$ where d' is the density of the fluid.

The specific gravity of melted waxes may be conveniently determined by means of a Westphal balance.

Floating Wax Ball Method. The specific gravity of a wax can be determined in the following manner. Spherical balls of wax are made by pouring the melted test sample into a test tube of ethanol heated to 50°C. A capillary tube may be used for introducing the drops of wax into the ethanol. These wax balls are then immersed in standard ethanol-water mixtures of known densities. It is necessary to determine the point at which the balls rise, and the point at which they sink. The arithmetical mean of the densities of the two ethanol mixtures is the specific gravity of the wax. The accuracy of this method, however, is open to severe criticism. It certainly is not accurate to more than the third decimal place.

Durometer Hardness. The hardness of a wax may be expressed in units ranging from 0 to 100. Generally speaking, the waxes have a range of 20 to 100 durometer units. The durometer is a small instrument fitted with a blunt pin connected through a spring to a pointer on a dial (Figure 23). It is graduated into arbitrary units known as "durometer units." Hardness is measured as resistance offered by the specimen to the penetration of the blunt pin. Temperature is maintained in an air bath provided with an air-motor-deriven fan for good circulation, and with electric heaters regulated by means of a rheostat and thermoregulator.

Although the durometer is designed to be hand-held during the test, it was found that far more consistent results could be had by using a suitable mechanical holding and releasing device. For this purpose a cylindrical lead weight (1¼ in. diameter x 4 in. long, weight 1350 g including shaft) is connected by a steel shaft to the knurled knob on the durometer. The steel shaft slides freely through a guide mounted on the wall of the constant temperature box, and the whole assembly may be raised or lowered by means of a heavy cord extending through the top of the box. A steel plate provided with leveling screws is furnished as a support for the sample.

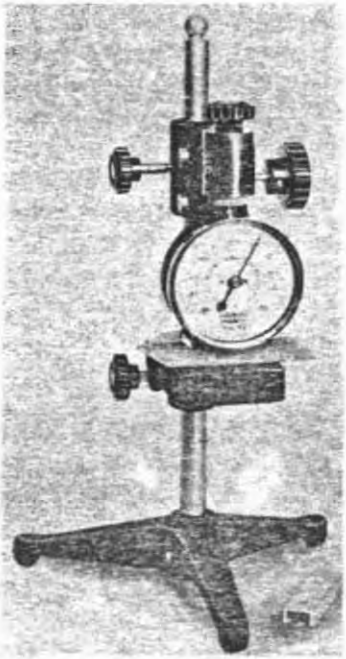
Molds, of carefully machined brass, are used to obtain a sample cake of convenient size and shape—about 3 in. square x ¾ in. thick, with flat, parallel faces.

Procedure. The sample is melted and molded in the special mold. When solid, it is removed from the mold and placed in the constant temperature

bath and maintained at the test temperature for at least one hour, assuming the sample to be at or near room temperature.

Details of handling the instrument and making the measurement are given by the Shore Instrument & Manufacturing Co., Jamaica, N. Y. Observations are made on the durometer every five seconds and are continued until the value falls off the same amount for each of three successive readings. The point at which the fall at constant rate begins is taken as the durometer hardness.

Penetration Test. The penetration test is one that measures the depth to which a needle with a definite top load penetrates the wax sample. Where



Courtesy The Shore Instrument & Mfg. Co., Jamaica, N. Y.

FIGURE 23. Round style durometer "A-2". Both quadrant style and round style conform to ASTM D 676–49 T specifications for testing hardness. Correct method of handling instrument to check calibration on test piece is shown.

FIGURE 23a. Round style durometer "A-2" mounted on stand. The cylindrical weight shown at top of the instrument simulates the hand pressure that would be used without the mechanical holding and releasing device. The knob over the weight permits a very careful adjustment so that the flat base of the durometer will be on a perfect level with the surface of the wax specimen. The blunt pin in the base is not shown here

the conditions of test are not specifically mentioned, the load, time, and temperature are understood to be 100 g, 5 sec, 25° (77°F) respectively, and the units of penetration to indicate tenths of a millimeter. Details for the operation of the instrument (see Figure 24) are supplied by the manufacturers of the instrument.

The penetration test is particularly well adapted for microcrystalline waxes, and is more reliable than the durometer test in determining hardness. The penetrometer readings on highly crystalline materials such as spermaceti are not reliable, and the durometer must be resorted to in order to secure a proper measurement of their hardness.

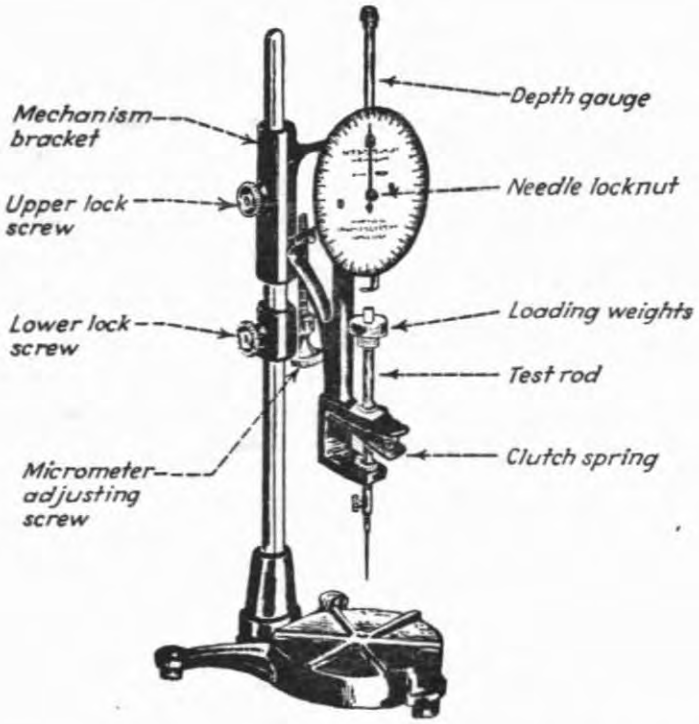
The relation between the values obtained by durometer hardness tests and those by penetrometer tests may be roughly correlated as follows:

Durometer at 25°C	Penetrometer #14 Needle 100 g/5sec/25°C
100	0–1
95	2
92	3
88	4
80	6
72	8
58	12
46	16
35	20
25	24
20	26

Durometer readings of below 20 are too uncertain to be of value. Penetrometer readings of very hard waxes are more accurate when taken with a 200-g instead of a 100-g test weight.

Shrinkage of Waxes. A molten wax shrinks uniformly while liquid until the temperature approaches the solidification point when the shrinkage may become very pronounced. Conversely, waxes in the solid form expand at a fairly uniform rate until the temperature approaches the melting point, whence they expand more rapidly until the wax is entirely melted. If a curve is drawn of the expansion against the temperature the irregularity in such a curve will be most pronounced at the melting point.

Microcrystalline waxes having a penetration value of 15 or more show the least change. Peculiarly, "I. G. Wax Z" (synthetic hydrocarbon wax) shows no detectable change in its transition from solid to liquid. The coefficient of cubical expansion of this wax is 0.000645 throughout a wide temperature range. Candelilla wax when melted shrinks to about the same extent as a hard paraffin wax. Ozocerite of Boryslav, Poland is devoid of shrinkage. Carnauba wax changes its rate of expansion pronouncedly when liquid; its expansion is 2½ times as great as in the solid state. Carnauba-paraffin wax mixtures 50:50 show the greatest variation from normal in



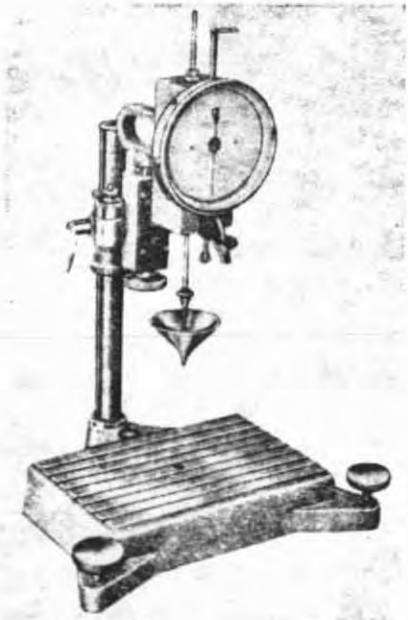


FIGURE 24. *above:* Diagram showing essential parts of the penetrometer. *right:* "Precision" penetrometer. Instrument conforms to the Standards (1951) for the testing of hydrocarbon waxes used for electrical insulation, ASTM D 1168 - 51 T.

Courtesy Precision Scientific Co., Chicago, Ill.

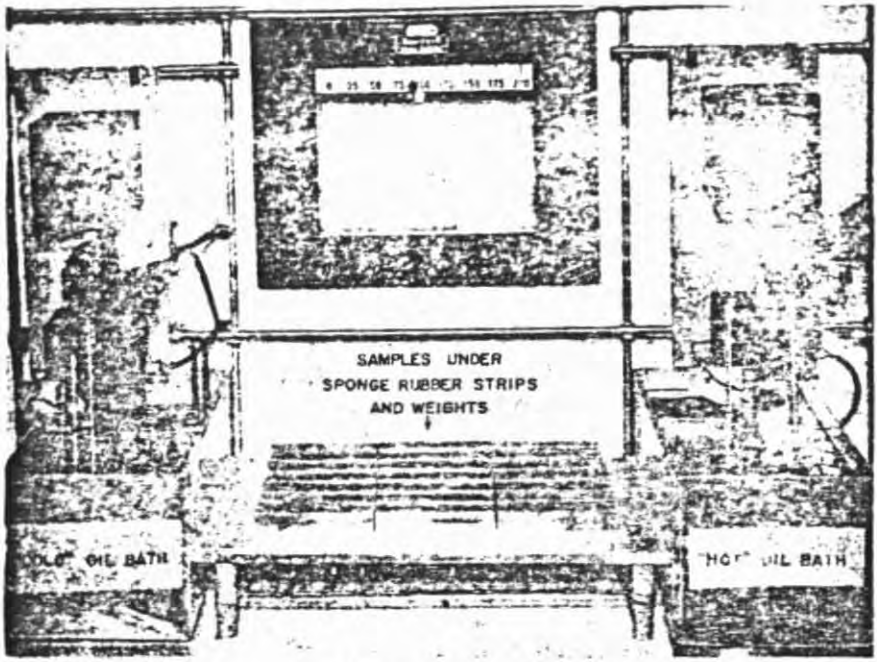
their contraction upon solidification[12]. Ouricury wax shrinks to the extent of 17 per cent of its volume upon solidifying, or more than carnauba wax. Beeswax shrinks only 9.6 per cent, or far less than paraffin wax. Koch[12] studied the effect of composition on the specific gravity of binary wax mixtures, and found it unsafe to compute the specific gravity of wax-mixtures as a mean of their components.

Refractive Index. A beam of light is more or less deviated or refracted in passing from air (or a vacuum) into a substance, and the ratio of the sines of the angles of incidence and of refraction is a constant at the boundary between the two media, i.e., $\sin i / \sin r = n$. The refractive index, n, of any substance is the ratio of the velocity of light in a vacuum to the velocity of light in the substance. Except for the thermal expansion effect, the refractive index is independent of temperature, but it varies with the wavelength of light. Therefore it is necessary to specify the wavelength at which any given measurement of n is made. This is usually done by means of a subscript; e.g., n_D indicates the refractive index was observed with the sodium D line.

The index of refraction of a wax may be determined by (a) the Pulfrich refractometer, (b) the Abbe refractometer, (c) the Zeiss butyro refractometer, or (d) the Amagat-Jeans oleorefractometer. Usually the refractive index is determined on the Abbe type of refractometer with water-jacketed prisms and provided with a special thermometer reading to 100°C. If the determination is made at 84°C (183.2°F), the result is reported as n_D^{84}; for example the refractive index of *dotriacontane*, $C_{32}H_{66}$, is n_D^{84} 1.4315.

Blocking Point Test. In evaluating the blocking point, or blocking temperature, of paraffin waxes the test is one in which a folded, waxed-paper strip is placed on a metal plate having a fixed temperature gradient over its length. The wax to be tested is coated on a standard paper, so that there is a surface wax load, according to Turner *et al.*[26], of 4 to 6 pounds per ream on one side, and 2 to 6 pounds per ream on the other. Test strips (1 x 36 in.) are cut from the waxed sheet. The test strip is folded back on itself, so that the heavier waxed surfaces face each other. The folded strip is then inserted between two unwaxed strips of paper and placed on a metal plate having a temperature gradient along its entire length. A sponge rubber pad (1 x ¼ x 18 in.) and a steel weight (1 x 1 x 11 in.) are placed on top of the test strip sandwich. After 17 hours on the blocking plate the samples are removed, cooled, unfolded, and visually rated. Farnham *et al.*[6] use only a 7-hr test period, since their test strips are heavily waxed (12–14 lb per ream machine coated).

The distance along the strip to the point which divides the blocked from the nonblocked zone is converted to the blocking temperature by means of a temperature calibration curve for the plate. By inspection a zone will be



Courtesy Standard Oil Development Co.
(Reprinted from "Modern Packaging," March 1952)

FIGURE 25. S.O.D. blocking-point test apparatus. A test sample between two unwaxed paper strips is placed on an aluminum plate, the temperature of which is varied from end to end. After contact with the plate for a prescribed period under pressure, the strips are removed, cooled, separated, and examined to determine areas where blocking has taken place.

found where the waxed surface is slightly disturbed; the low temperature end of this area is the "pick" point. Further toward the hot end of the gradient plate the point of complete blocking or sticking of the waxed surfaces will be seen; this is recorded as the "blocking temperature," e.g., 100/105 = pick/blocking temp.

On the S.O.D. (Standard Oil Development Company) blocking method the gradient plate (20 x 12 x ½ in.) is of aluminum and is linked with a "cold" oil bath at one end, and a "hot" oil bath at the other. The cold end is at 75°F and the hot end at 160°F. Farnham *et al.* prefer this type of heat control to the strip heater for blocking point determinations.

Tensile Strength Test. In the method usually employed the tensile strength is the average ultimate breaking strength of wax briquets, cast and tension-tested under specified conditions. The tensile strength apparatus is known as a tensiometer. Two vertical lead-screws drive a horizontal crosshead at constant speed by means of a motor through a suitable reduction

gear. To the crosshead is attached a Chatillon spring scale to which in turn is attached a clamp for holding one end of the sample to the instrument. The applied load is indicated on the dial of the spring scale. The elongation is read to the nearest $\frac{1}{100}$ inch on the vernier scale. The entire apparatus is mounted in a constant temperature box with the heating and cooling systems necessary to give reasonably constant temperature.

The mold is of a modified Dow design in which the sharp corners are removed from the inside shoulders. A small box used to hold the mold is made by bending $\frac{1}{64}$-inch sheet lead around a wooden block and folding the edges in such a manner as to make a tight one-piece container, which is easily removable from the sample when the wax has a solidified and cooled sufficiently to permit handling.

Viscosity. The property of a liquid which offers resistance to a change in shape is called *viscosity*. Since water is a mobile liquid it is often taken as unity in the standardization of instruments designed to measure viscosity. Such instruments depend on the determination of the rate of flow of the

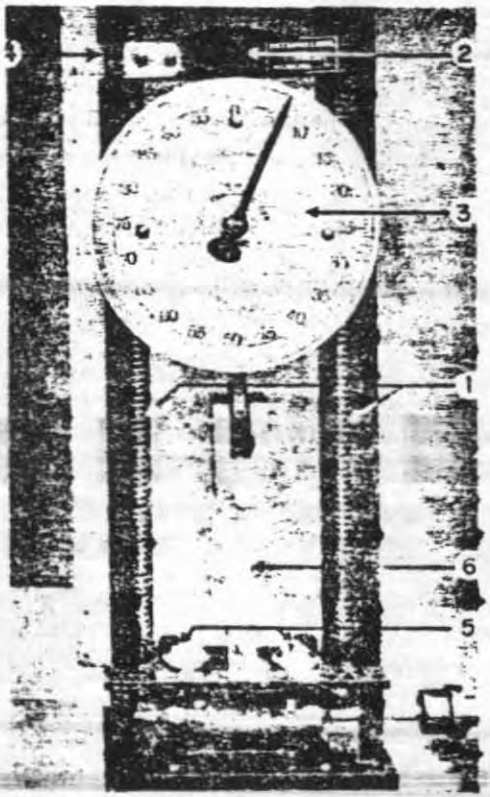


FIGURE 26. Tensile strength apparatus, or tensiometer. (1) lead screws; (2) crosshead; (3) Chatillon spring scale; (4) vernier scale; (5) dials for precision reading; (6) specimen of wax.

Courtesy Atlantic Refining Co., Phila., Pa.

liquid through a small aperture, or on the speed of a rotating element introduced in the liquid, the element being subjected to well-regulated constant pressure. The torque produced is directly proportional to the force required to make one portion of the liquid move over another. Viscosity is a measurement of internal friction.

There are many instruments used in determining viscosities. One is the Saybolt which depends on ascertaining the rate of flow through an orifice under well-controlled constant temperature conditions; another is the Stormer Viscosimeter which depends on a pulley with a weight attached to cause the rotating element to revolve in the liquid.

The Saybolt Standard Universal (SSU) viscosimeter method is fully described in specifications set forth by the American Society for Testing Materials. It is customary to determine the viscosities of petroleum waxes at 210°F (98.9°C) with readings in seconds.

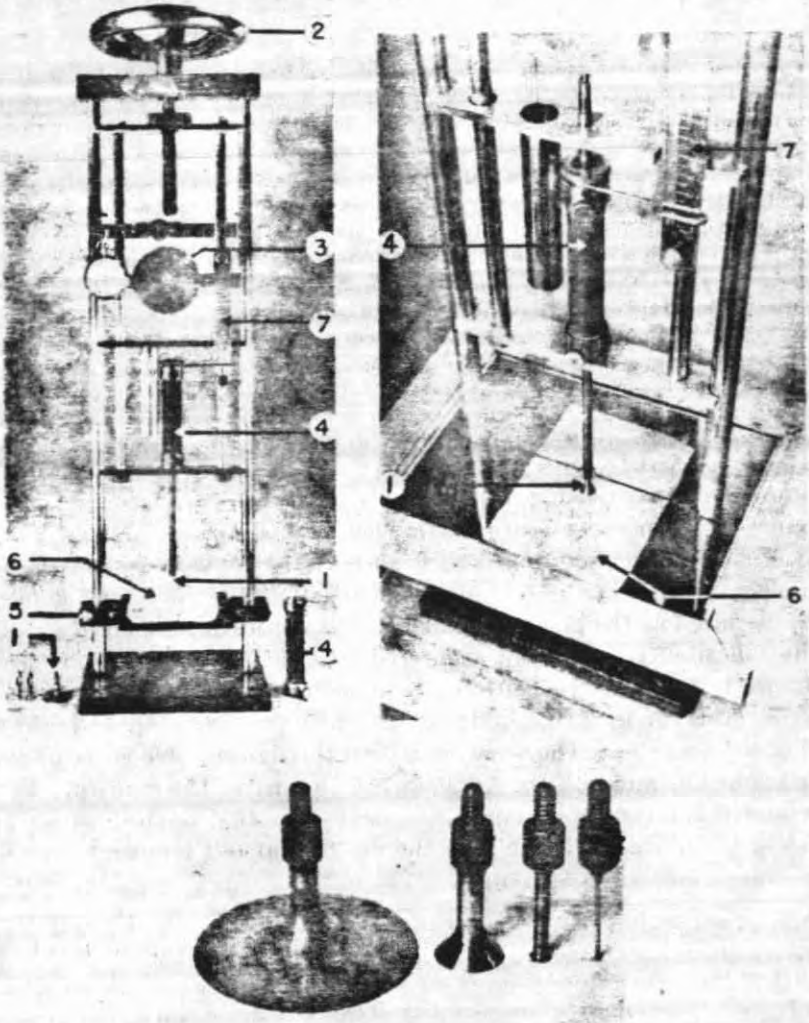
Kinematic Viscosity. SSU readings in seconds are convertible into the "units viscosity scale" which reads in *stokes* and is known as kinematic viscosity. For the purpose of avoiding fractional numbers kinematic viscosity is customarily expressed as *centistokes*. One centistoke equals $\frac{1}{100}$ stoke. This is a scale which has been coming into wide use by the petroleum refiner.

The relation between kinematic viscisoty and SSU viscosity at 210°F is illustrated by the following example:

Kinematic Viscosity (centistokes)	Equivalent SSU Viscosity (seconds)
2.0	32.8
2.5	34.6
3.0	36.3
3.5	37.9
4.0	39.4
4.5	41.0
5.0	42.6
5.5	44.2

Absolute Viscosity. To convert kinematic to "absolute viscosity" the centistokes are multiplied by the density (d') of the liquid wax and the result expressed as *centipoises*. One centipoise equals $\frac{1}{100}$ poise. The kinematic viscosity of a wax can also be read directly by the use of an Ostwald viscosimeter. Absolute viscosities may be read directly by the use of a Brookfield viscosimeter. Readings may be made over a very wide range, e.g., about 3 for a paraffine to 2000 cps for a polyethylene wax.

Consistency Test. Consistency is determined as the kilograms per square centimeter that it takes to compress a wax ½ cm by a suitable plunger. The determination is generally made with an Abraham consistometer which is provided with four plungers (1, 10, 100, and 1000 sq mm area). The consistometer is a vertical, manually operated mechanism so



Courtesy Atlantic Refining Co., Phila, Pa.

FIGURE 27. *left:* The Abraham consistometer. *right:* Details of the consistometer. *above:* The four plungers of 1, 10, 100, and 1000 square millimeter area, used for consistency test. (1) plunger; (2) hand wheel; (3) dial gage; (4) calibrated springs; (5) adjustable platform; (6) specimen of wax; (7) scale.

designed that a push-rod carrying plunger may be driven downward at a definite and controlled speed by turning a hand wheel. Means are provided to measure the downward movement of the push-rod and plunger on a dial gage. Also, by means of one or two calibrated springs and scale the pressure required to produce or maintain the downward motion may be measured.

The springs provide two ranges, one from 0 to 1 kg, the other from 0 to 12 kg.

Procedure. The test sample is cut or molded to a size convenient for testing as 3½ in. x 4½ in. x ¾ in. to 1 in. thick. If molded, it must be aged for 18 hours; it is then placed on the adjustable platform of the consistometer and adjusted so that the upper surface of the wax is level and about ¼ in. below the glass of the partition. A suitable plunger (generally one with 100 sq mm area) and spring are selected and placed in the apparatus. The plunger is then lowered until it just touches the surface of the wax. At this point the pointer on the gage indicating vertical travel is set to zero. A stop watch is started and hung on a hook provided for the purpose. By means of the hand wheel, the plunger is moved downward at such a rate that the pointer on the dial gage and the second hand on the watch move at the same speed. When moving at this rate, the plunger is being lowered at 1 cm per minute. Readings of the pressure required are made and recorded every $^{5}/_{60}$ cm, and plotted on semi-log graph paper. As the value at the $^{30}/_{60}$ reading (½ cm penetration) has been found by experience to be the most reproducible, that value is taken as the consistency after application of corrections, if necessary. Results obtained with other plungers are converted to values corresponding to the No. 100 plunger (100 sq mm) by suitable conversion factors.

Bending Test. Bending tests are only applied to paraffin waxes or wax mixtures used in paper coating, etc. One method applies pressure at the end of a wax sheet, causing it to bend over the rounded end of the test sample platform. The results are reported as *degrees bend*, and *grams* of force required at the point of breaking. The apparatus employed is essentially a flexibility instrument connected by a rack with an Abraham consistometer, replacing the platform, base, and plunger of the latter. A pair of cross arms carries a cross-rod through which pressure is applied near the end of the wax sheet. The arms are moved through suitable gears by pressure applied by means of the Abraham consistometer. The entire apparatus is mounted in a constant temperature air bath, so that the test sample and bending tester are inside the bath and are held at test temperature, while the controls and scales are outside.

Procedure. Sufficient sample to produce a sheet 1.2 mm thick (35 g for a 6 × 8½ in. glycerin surface) is melted and poured on the surface of glycerin which has been heated 10 to 20°F above the melting point of the wax. The proper temperature for pouring may be easily ascertained by dropping a small chip or shaving of the wax on the cool glycerin; then heating slowly with constant stirring until the wax just melts. At this point, the heat source is removed and the melted wax poured onto the surface. Bubbles must be removed, and the wax and glycerin allowed to cool to room temperature (or lower, if necessary) after which the wax sheet is removed and cut into pieces 2 × 3¼ in. The test sample after sheeting should be aged overnight at near the test temperature.

The sample is placed and clamped on the platform, and the cross-rod adjusted to just touch the upper surface of the sample. At this point the needle on the dial gage for penetration, as well as the scale showing applied pressure, are set at zero. Pressure is then applied by means of the hand wheel so that the rack moves downward at a uniform rate of 1 cm per minute as shown by the dial gage. Readings of penetration

For details of the ways and means of measuring *K*, *PF*, and other dielectric measurements, and the calculations involved, consult *A.S.T.M. Standards*, 1946, Part III-B, Non-Metallic Materials: Nos. D149–44; D150–46T; D237–46; D495–2.

The precise value obtainable for the dielectric strength of a specimen of wax will depend on such factors as the type of voltage (d.c. or a.c.), frequency, duration of application, rate of rise, temperature, humidity, shape and size of electrodes, and the nature of the surrounding material. Metallic electrodes are applied to the dielectric, and the maximum voltage gradient varies inversely with the radius of the electrode and becomes more uniform as the area of the electrodes in the condenser is increased. The a.c. instruments customarily used operate at various frequencies, namely below 10^8∼/sec, or 10^8–10^{10}∼/sec, and the resulting *K* values are noticeable higher for the lower frequency when the wax specimen contains moisture.

Differences in the results for *K* value and *PF* variations with change in A-C frequencies is illustrated as follows: A plastic insulation composition comprising polyethylene, microcrystalline wax, and zinc stearate had a *K* value 2.31 and *PF* of 0.00006, both at 1000 cycles; and a *K* value of 2.11 and *PF* of 0.00104 at 1×10^6 cycles, both at 25°C, which make the composition suitable for use at radio frequencies.

Solubility Tests on Waxes. In determining the solubility of a wax in a specific solvent, it is sometimes advisable to proceed qualitatively, since the test sample may be very soluble in the solvent. About 1 g of the pulverized test sample is added to 10 ml of solvent slightly warmed, shaken, and allowed to stand for ½ hour, after which it is shaken again. If wax appears to have completely dissolved, the amount of wax taken for quantitative determination should be at least doubled in the analytical test procedure described below. For example, candelilla, carnauba, and ouricury waxes are soluble to the extent of less than 10 g in 100 g benzene, whereas japan-wax and spermaceti have a solubility greater than 50 g in 100 g benzene. All waxes have low solubilities in alcohol.

The procedure to be followed in making solubility tests is to dissolve 5 g of the finely pulverized wax (freed from moisture by vacuum drying) in about 50 ml of the solvent in a flask of 100-ml capacity. The solvent plus wax should be carefully weighed, and solvent lost through evaporation must be later replaced. The flask is then stoppered and shaken thoroughly; the stopper is now untightened, and the flask gently warmed to a temperature slightly above (<3°C) the test temperature, then tightly restoppered and shaken every ½ hour for 2 hours. After this, the temperature of the wax solution must be brought down to the precise test temperature (25 or 37°C) and sufficient solvent at the same temperature added by pipette until the original weight is reached. The flask is then shaken and allowed to

stand for one hour. A 25-ml portion is withdrawn and placed in a tared glass-stoppered circular weighing vessel with straight wall sides, or weighing bottle. The vessel is unstoppered after weighing and the solvent allowed to evaporate slowly in a vacuum oven. When dry the wax residue is weighed.

$$\text{Solubility at } t^\circ = \frac{\text{wt. of residue} \times 100}{\text{wt. of wax solution} - \text{wt. of residue}}$$

Solubility determinations should always be made in triplicate, and unless the results are too wide apart the solubility is taken as the mean of the three values.

Physical Tests for the Identification of Wax Components and their Molar Constants.

Determinations of the setting, resolidification, and melting points afford one means of determining the purity of a wax component; often these determinations are made on derivatives of the component. Boiling points are determined either on the isolated wax component or on a derivative, such as the methyl ether of a wax acid. Specific rotation is determined on sterols or other optically active substances. Molecular distillation is employed in separating wax components; substances isolated in a state of purity are subjected to a molecular weight determination, for which there are several methods. Hydrocarbons in petroleum waxes are differentiated as normal paraffins, isoparaffins, cycloparaffins, and alkyl benzenes by mass spectrometer analysis, and to some extent by their aniline points.

Molar determinations include molecular rotation as an expression of optical activity; molar volume; and molar refractivity.

Identification of Crystalline Substances. In the identification of pure organic substances derived from waxes, determinations are made of setting, resolidification, and melting points. The setting or freezing point (s.p.) requires several grams of material and denotes the point at which the falling temperature hesitates or remains constant for a short period before it drops further again. The melting point (m.p.) and the resolidification point (r.p.) are made on a fraction of a milligram of substance fused in a convenient position on the side of a capillary tube 3 to 4 mm in diameter, sealed at one end. The tube is placed in the bath, the crystals brought into focus of a telescope, and observations of melting point (m.p.) and resolidification point (r.p.) are recorded. The r.p. is the temperature at which the partly molten specimen in the capillary tube commences to solidify when the temperature is lowered very slowly. The values found for r.p. should be close to those found for s.p. Francis and Piper[8] used these methods in their determination of the melting points of the *n*-aliphatic acids and esters. For

example, they found the following values:

Carbon Content of Acid	S.P.	R.P.	M.P.
14	53.65	53.9	54.4
16	62.60	62.4	62.9
18	69.39	69.2	69.6
22	79.70	79.6	79.95
24	83.90	83.8	84.15
26	87.41	87.2	87.7
34	98.00	97.8	98.2

Similar slight differences were found for the methyl esters and the ethyl esters.

Boiling Points. Boiling points are ordinarily determined by placing the tip of the thermometer bulb *just below the outlet tube* of the distillation apparatus which consists of a 100-ml distilling flask, resting on an asbestos shield, 3 mm thick and having a hole 2.5 cm in diameter cut in its center. Fractional distillations may be made with a Fenske-type electrically heated helix-pack, 12 × 530 mm column on still head and condenser, also electrically heated.

Fractional distillation of the wax acids is more easily carried out on the methyl ether derivatives. The wax acids in this case are treated with methanol and sulfuric acid, some diazomethane is added to facilitate the reaction in producing the methyl ethers in quantitative proportions. To recover the acids from the methyl ethers the latter are saponified with sodium hydroxide, the sodium soaps precipitated with barium chloride, and the acids then released from the benzene-washed dried barium soaps with hydrochloric acid. Alcohols from unsaponifiable matter must first be oxidized to acids and then converted to the methyl ether derivatives.

Specific Rotation. The optical activity of a compound may be expressed as *specific rotation*, $[\alpha]$, or molecular rotation M. In determining the specific rotation by means of a suitable polariscopic instrument the density of the liquid, the wavelength of light used, and the temperature must be taken into account. The specific rotation, $[\alpha]$, at a temperature, t, and definite wavelength of light is expressed as $[\alpha]_\lambda^t = rv/ld$, where r is the observed polarimetric rotation in degrees, l, the length of the column, and d, the density of the substance if liquid. In the case of a solution, $[\alpha]_\lambda^t = rv/lp$, where v equals the volume in cubic milliliters, and p the grams of substance contained in v volume of the solution. Since a sodium flame, D, is the customary spectrum source of illumination, the specific rotation may be customarily expressed as $[\alpha]_D^t$.

For example, the specific rotation, $[\alpha]_D^{25}$, of cholesterol is determined in solution in dehydrated alcohol containing in each 100 ml 2 grams of cholesterol, and using a 200-mm tube. Assuming the reading of the angular rotation of the polariscope is $-118.0°$ for a specimen of cholesterol in solution,

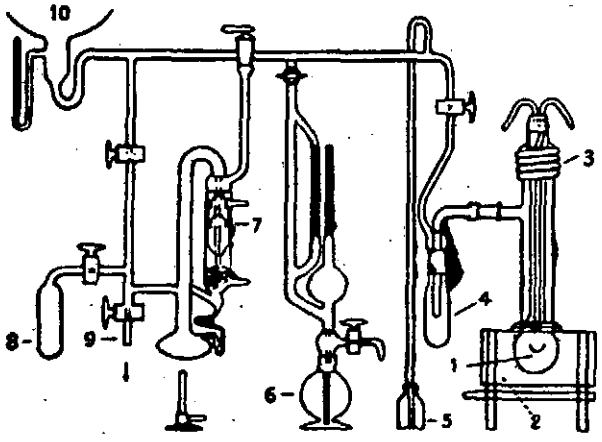
then

$$[\alpha]_D^{25} = \frac{100 \times 118^\circ}{200 \times 2} = -29.5^\circ$$

The molecular rotation is expressed as $[M]_\lambda^t = m/100 \cdot r v/lp$ where m is the molecular weight of the substance. The factor 100 is used simply for convenience of expression.

Molecular Distillation. There is a wide variation in molecular weights and in vapor pressures of the constituents of waxes; esters vs. hydrocarbons, free acids, and alcohols. Therefore we must expect a great difference in the chemical composition of the first and last fractions in the distillation of these complex mixtures.[9]

Various kinds of equipment have been devised to fractionate wax at predetermined intervals under a rising temperature with vacuums ranging from 30 microns down to 0.005 micron pressure. Findley and Brown[7] (1953) employed distillation apparatus consisting of two still pots (7 cm and 12 cm diam.). The condensing heads could be removed whenever a desired fraction had distilled, and be replaced with clean ones for further distillation while the first fraction was weighed and recovered. The still pot was equipped with metal head, brass washers, and magnetic stirring bar. The still pot was heated in a Wood's metal bath in a nonmagnetic stainless steel



From "Petroleum Refiner," 22, 9 (1943)

FIGURE 28. Diagram of arrangement for high vacuum distillation, illustrating the principle of the molecular still used by Carothers and his co-workers. (1) distillation vessel; (2) aluminum block with spherical depression, electrically heated; (3) circular water condenser; (4) receiver to condense cracked products; (5) barometer; (6) Macleod manometer; (7) mercury pump; (8) receiver cooled with liquid air; (9) connection to oil pump (not shown); (10) large flask used as a pressure equalizer and for vacuum storage.

dish resting on a small electric heating coil insulated underneath with asbestos. Tap water was circulated in the condenser head of the still pot.

Preparatory to distillation the solid sample is introduced into the pot and the system flushed with nitrogen. The hot (100°C) metal bath is then raised to melt the sample. The stirrer is started and the forepump turned on; one should stir instantly to lower the pressure in the system slowly, preventing spattering of the wax. The temperature is then raised and the distillation begun by further lowering the pressure with the diffusion pump. Fractions are removed from the head with hot benzene. Fractions may be made at 150 ± 10, 250 ± 10°C, or other predetermined temperature.

Molecular Weight Determinations

(1) *Ebullioscopic Method.* The effect of a dissolved substance on the vapor pressure of a liquid was first observed by the rise it produced in the boiling point. It follows that the presence of a dissolved substance lowers the vapor pressure; this law of change was concisely stated in the formula first proposed by Raoul:

$$\frac{p - p'}{p} = c\,\frac{n}{N - n}$$

where p is the vapor pressure of the pure liquid, p' is the vapor pressure after the addition of the substance, c is a constant nearly unity for dilute solutions, n is the number of molecules of the dissolved substance, and N the number of molecules of the solvent. Transforming the equation to a useful form for calculation of molecular masses, it becomes

$$M = \frac{sp'g}{Sp - p'}$$

where the molecular mass of the dissolved substance may be found when the lowering of the vapor pressure is known. In this equation s is the mass of a molecule of solvent, g the mass of dissolved substance, and S the mass of solvent. The equation may also be written in a different form when employing the volume of solution in ml and taking into account the barometric pressure, and convenience of measurement of p–P':

$$M = \frac{Kg}{LV} \times 1000 \times \frac{B}{760}$$

where $L = p$–p' in mm expressed as difference in liquid gage levels, V = volume of solution in ml, B = barometric pressure, and K is a constant representing lowering of the vapor pressure in mm of the boiling solvent that would be caused by the presence of 1 mole of solute in 1 liter of solution at normal pressure.

The apparatus used by Menzies[22] in evolving the foregoing equation consisted of a boiling jacket for the pure solvent connected by a short length of rubber tubing with a small reflux condenser, and a graduated inner tube furnished with a pressure gage tube and closed at the top by a glass stopper. When the rubber connection is close by a pinchcock and the stopper removed, the vapor of the boiling solvent must escape by blowing through the gage tube into the inner tube. The solution whose vapor pressure is to be determined is contained in the inner tube and the measurement is made in terms of the difference in level of the solution in the gage tube and the inner tube. Since the density of the liquids ordinarily used are low compared with Hg, the pressure may be measured with considerable accuracy, thus permitting the use of very dilute solutions.

(2) *Ebulliometric Method.* The molecular weight M_u of the unknown can be determined by measuring the rise in boiling point of a liquid (benzene, toluene, etc.) when the solute is added in small quantity (e.g. <1%). Measurement of the rise t is made by an ebulliometer as designed by Menzies-Wright, or by a modified form which employs a differential thermometer (Kitson and Mitchell) from which readings can be taken in mm instead of °C. The basic formula for calculating the molecular weight as proposed by Swietoslawski (1945)[25] is

$$M_u = \frac{w_u \times M_s \times \Delta t_s}{w_s \times \Delta t_u}$$

where w_u and w_s are the weight of the standard and unknown added, M_s is the molecular weight of the known, and Δt_s and Δt_u are the observed temperature changes of the known and unknown.

The weight and subsequent change of temperature (expressed conveniently as mm rise in the capillary arm of the thermometer) for a pellet of standard and for a pellet of unknown, are the four experimental values required to calculate the molecular weight. By adding a pellet (100 mg) of standard before and after the addition of the sample, standard data can be averaged before substitution in the formula, when the simplified equation becomes

$$K = M_s \times \Delta t_s$$

where K is the constant value for the standard obtained by averaging a number of calibrated runs.

Then the molecular weight for each addition may be computed from

$$M_u = \frac{K \times w_u}{\Delta t_u}$$

In the modified Menzies-Wright ebulliometer[11] the differential thermometers are suitable for filling with liquids of various boiling points. Operating

the thermometer at a temperature above the boiling point of the filling liquid increases the sensitivity of the instrument. Materials of very high molecular weight are run in xylene with either the *p*-xylene or toluene thermometer. The ebulliometer has a sealed-in boiler (30 ml), and a 4-jet pump.

(3) *Cryoscopic Method.* The diminution of the vapor pressure of a liquid by the presence of a substance in solution has the effect of lowering the freezing point. This is expressed mathematically by the Van't Hoff formula

$$\Delta r = \frac{Rr^2n}{LN}$$

where R is the constant in $pv = mRr$; r is the lowering of the freezing point; n, the number of molecules of dissolved substance; L, the latent heat of fusion per unit mass; and N, the number of molecules of the solvent.

In the applied method the freezing point of a substance is ascertained, and a gram-molecule of a substance of known molecular weight is dissolved in a known weight, and hence in a known volume, of the solvent. This lowers the freezing point a certain amount, which is always the same for the same solvent, no matter what the substance may be, provided that the volume of solution, containing the gram-molecule is the same.

The simplified formula is

$$M = \frac{K_s w_s}{\Delta T}$$

where K_s is a constant derived from

$$K_s = \frac{\Delta T}{c_1 M_s},$$

T is the temperature lowering, c_1 is the concentration of the solution, M_s is the molecular weight of the standard, and w_u is the weight of the unknown.

Findley and Brown[7] determined molecular weights of wax fractions of carnauba, caranda, candelilla, ouricury waxes, and beeswax by the Rast method of freezing point depression. Cholesteryl palmitate and behenic acid were used to determine the molecular depression constants.

(4) *X-Ray Diffraction Method.* Molecular weights of waxes may be determined by x-ray diffraction if the substance is crystalline, and if the unit cell of a crystal contains a whole number of molecules. The number of molecules usually small in an orthorhombic crystal will be almost the power of 2, in the tetragonal a multiple of 4, etc. A single crystal weighing 10^{-6} gram can be used.

$$M = \frac{vd}{n \times 1.66}$$

where n is the number of molecules in the unit cell, d = density, v = volume of crystal, and mass of H atom (at. wt. 1.0008) is 1.66×10^{-24} g. Therefore weight of cell contents referred to oxygen as 16 can be obtained by dividing by 1.65×10^{-24}. Since 1 Å = 10^{-8} cm, 1 Å^3 = 10^{-24} ml. The 10^{-24} is eliminated if the computation is carried out in angstrom units, and the equation for the molecular weight, M, of the material becomes that given above. The value for n will be close to one of the possible integral values if the approximate value is put into the equation and the equation is solved for n.

(5) *Light Scattering Method.* Molecular weights can be determined by light scattering, based on the following principles: (a) measure of the intensity of scattered light, (b) some measure of the dissymmetry of intensity in forward and backward direction, and (c) a measure of refractive index difference between solvent and solution, all as a function of concentration and at known wavelengths. The refractive index of the pure solvent must also be known. Light of known wavelength is most conveniently procured by filter isolation of a line in a line-spectral source.

(6) *Analytical Constants Method.* Mean molecular weights of the esters and acids of waxes can be calculated from the ester numbers and acid numbers as has already been described under such determinations. The mean molecular weight of hydroxy acids may be determined from their hydroxyl number provided other acids are absent. The mean molecular weight of alcohols can be calculated from their hydroxyl number, equations for both of which have already been given. These equations are predicated on the assumption that the esters are simple normal esters or simple monohydroxy esters, and the alcohols are straight-chain monohydric alcohols.

When an approximation of the molecular weight is made from the acid, ester, or hydroxyl number as the case may be, it is necessary to supplement it by an ultimate analysis for C, H, and O. The empirical formula alone will not suffice because obviously $C_aH_bO_c$ has the same percentage composition as $(C_aH_bO_c)_n$. The mean molecular weight of hydrocarbons can be determined by ultimate analysis for C and H.

(7) *Viscosity Method.* The molecular weight of high polymers may be determined by the Staudinger relation $[\eta] = K_m P$ where P is the degree of polymerization as determined by osmotic pressure, $[\eta]$ is the intrinsic viscosity (expressed in centistokes), and K_m is a constant.

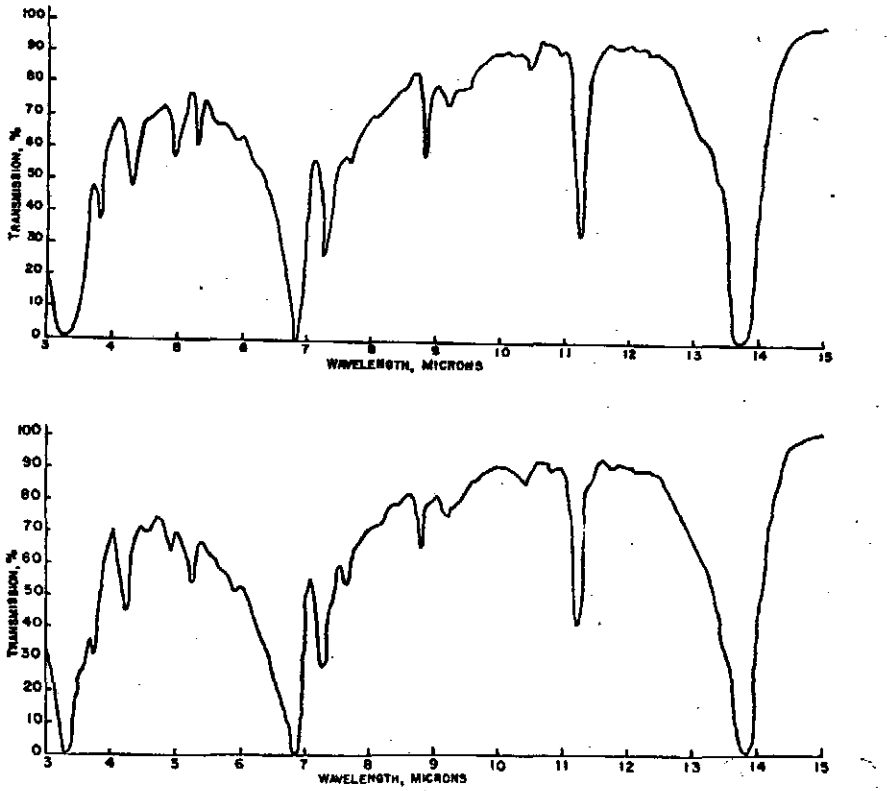
$$[\eta] = KM^a$$

As the viscosity within a polymer series increases largely with the molecular weight, it can be utilized for molecular weight determinations.

Mass Spectrometer Analysis. Mass spectrometer analysis of paraffin waxes, according to Turner, Brown, and Harrison[26], gives information simultaneously on two important features of a wax: the molecular weight distribution, and the molecular types present. For convenience in studying,

the data obtained may be shown graphically, plotting weight per cent on the ordinate against number of carbon atoms on the abscissa. These investigators in their determination of the composition of waxes (1955) used a standard Consolidated Engineering Corporation Model 21-103A analytical mass spectrometer which was modified for high temperature work.

A means for examining the mass spectra of heavy hydrocarbons and for determining and correlating structure and special characteristics of those in the C_{14}–C_{32} range has been described in detail by O'Neal, Jr., and Weir, Jr. These investigators employed a standard Consolidated Model 21-102 analytical mass spectrometer which they modified by decreasing the ion slit widths and exit slit, so as to scan satisfactorily and resolve the mass scale up to about *m/e* 600. [O'Neal, M. J., Jr. and Weir, T. P., Jr., *Anal. Chem.*, **23**, 630 (1951)]. The composition of paraffin waxes of various tensile

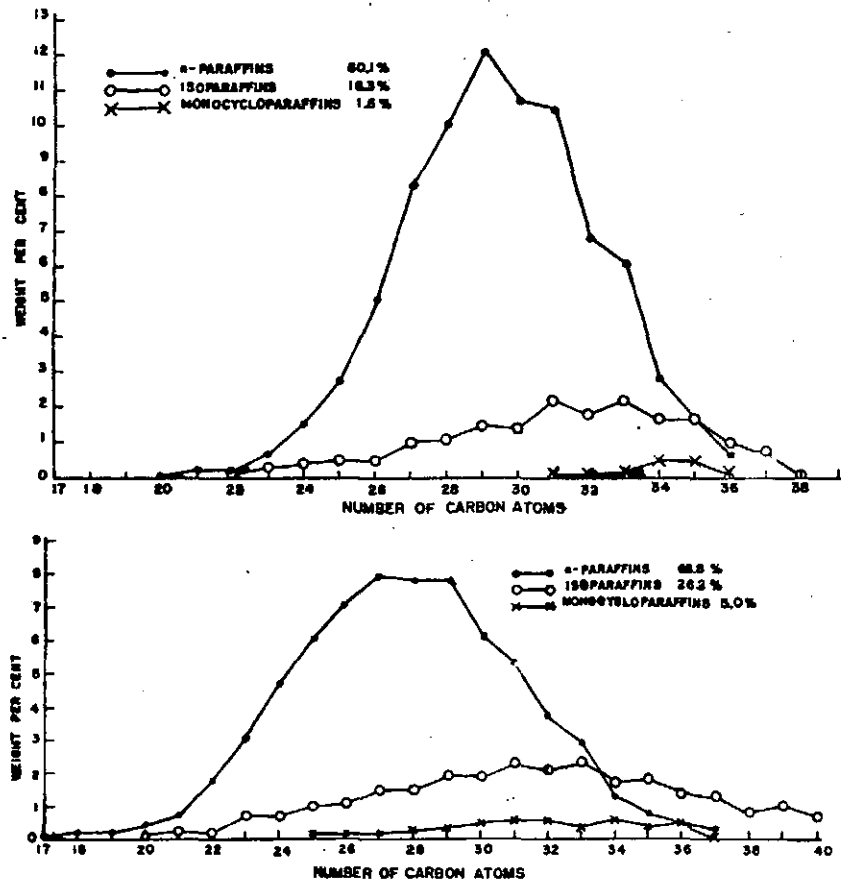


Courtesy The Atlantic Refining Co., Phila., Pa.

FIGURE 29. Infrared spectrometric analyses of two of the author's specimens of Asiatic paraffin wax. Analyses were done with a Beckman Model IR_2 Spectrometer. *Top:* 148/150 AMP grade. *Bottom:* 163/165 AMP grade.

strengths as recently determined by Edwards was with a similar instrument, Model 21-103 modified for high mass use [Edwards, R. T., *Ind. Eng. Chem.*, **47**, 2555–25558 (1954)].

The composition of samples of Asiatic paraffin wax (produced in 1938 but analyzed in 1955) as shown by the plots in Figure 30, are based on the assumption that the isoparaffins present have melting points of those of normal paraffins containing six fewer carbon atoms, and that the monocycloparaffins have melting points equal to those of normal paraffins containing three fewer carbon atoms.



Courtesy The Atlantic Refining Co., Phila., Pa.

FIGURE 30. Mass spectrometric analysis of the specimens of wax described under Figure 29. The mass spectrometer used was a Consolidated Engineering Corporation Type 21-103, with a sample-handling system modified for high temperature analysis. *Top:* 148/150 AMP grade. *Bottom:* 163/165 AMP grade. Latter proved to be a mixture of 137.5°F AMP and very high melting paraffins.

Crystal Spacings From X-Ray. The following description of procedure of determining crystal spacings (A, B, or C) in Angstrom units (Å) is taken from Francis and Piper[8].

"To obtain x-ray photographs, flakes of the material are pressed in a thin layer onto a glass strip 5 mm × 1 cm, using the minimum pressure to cause adhesion. Heavy pressure or rubbing tends to distort the crystals, causing broad lines on the reflections. The plate is mounted vertically with its coated face in the axis of the rotation of the x-ray spectrometer, and parallel to a narrow beam of x-rays passing through the spectrometer slits. The beam is supplied by any suitable tune with a copper anticathode and is filtered by a thin nickel foil. The specimen is rocked to and fro by a cam mechanism, and the reflections are recorded on a strip of photographic plate or film placed perpendicularly to the x-ray beam and 5 cm from the rotation axis of the spectrometer. Reflections are recorded on both sides of the central beam, and the angle of rock is varied to suit the type of record required—about 10° for poor material, 20° for good. The spacings are calculated in the usual way for the Bragg law

$$n\lambda = 2d \sin \Theta$$

where n is any integer, d the spacing between the lattice planes parallel to the plane considered, and Θ the angle made by the incident ray with this plane.

"Exposure times vary from one hour to six hours or more with a Phillips type of tube running at 10 m.a."

Tables are given by the authors for the crystal spacings both B and C for the acids of even carbon content ranging from C_{14} to C_{32}, for C_{46}, and for those of odd carbon content with 17 to 29 carbon atoms. Values for the crystal spacings A are also given for their methyl and ethyl esters.

The spacings for CH_2 groups in the fatty acids vary in length according to the preparation of the specimen examined. If the specimen is a melt, the value for the length of the bond between adjacent carbon atoms is referred to as the *C* value. For the straight-chain fatty acids and alcohols the *C* value is 1.09×10^{-8} cm, equivalent to 1.09 Å. Where the specimen has been obtained as a result of very slow crystallization from a polar solvent such as ethanol, the crystals are distinctive; the value for CH_2 is 1.21 Å, and is known as the *B* value. If the specimen is the result of rapid crystallization, or contains impurities, the spacing measurement will be of the order 1.4 Å, which is referred to as the *A* value. Usually the spacing values are recorded as *C* or *B*, or both *C* and *B*. Crystals from a polar solvent are usually recrystallized from a nonpolar solvent.

In making a mount it is sometimes advisable to first compress the powder to a pellet, When the specimen is recorded as "pressed on slide."

Molar Volume. Molar volume is the volume occupied by one mole of a substance, and is derived by dividing the molecular weight by the density of the substance. Specific volume is the reciprocal of the absolute density.

Certain substances such as fatty acids, alkyl esters of fatty acids, etc. exhibit polymorphism, that is, they crystallize out in more than one solid or polymorphic form, and therefore the molar volume in the solid state is related to the cross-section area of the unit cell of the crystal for any given polymorphic form. If, for example, the molar volume in the solid state is known and the length of the unit cell is determined by x-ray measurement or other suitable means, then the cross-section area of the unit cell of the crystal can be calculated.

Since the cross section of a single molecule in the crystal of any fatty acid is 23.8 Å, changes in molecular volume must be due entirely to changes in chain length. The molar volume of a fatty acid, C_4- to C_{18}-chain length, can be calculated from the equation $V_m = 17.25n + 28.88$, where n is the number of carbon atoms in the chain, and the temperature of the liquid is 80°C[5].

Molar Refractivity. When the values of density and refractive index of a normal saturated fatty acid at the same temperature (80°C) are known, the molecular refractivity R_m can be calculated according to the Lorenz-Lorentz[16, 17] equation:

$$R_m = \frac{n^2 - 1}{n^2 + 2} M \times \frac{M}{d}$$

For example, the refractive index (n_D^{80}) of stearic acid is 1.4299; its molecular weight is 284.47, and its density (d^{80}) is 0.8390, whence the molar refractivity R_m would be calculated as follows:

$$\frac{(1.4299)^2 - 1}{(1.4299)^2 + 2} \times \frac{284.47}{0.8390} = 87.69$$

The molar refractivities of the normal saturated fatty acids C_{12}, C_{14}, C_{16}, and C_{18}, are 59.7, 69.0, 98.3, and 87.7 respectively[5].

References

1. Andre, E., and Maille, M., *Bull. soc. chim. France*, **1947**, 215–217.
2. Benedikt, M., and Ulzer, F., *Monatsh.*, **8**, 40 (1887).
3. Benham, G. H., and Klee, L., *J. Am. Oil. Chemists' Soc.*, **27**, 127–129 (1950).
4. Berg, R., *Chem. Ztg.*, **31**, 337–339 (1907); *ibid.*, **33**, 885–887 (1909).
5. Dorinson, A., McCorkle, M. R., and Ralston, A. W., *J. Am. Chem. Soc.*, **64**, 2739–2741 (1942).
6. Farnham, H. M., *et al.*, *Modern Packaging* (March 1952).
7. Findley, T. W., and Brown, J. B., *J. Am. Oil Chemists' Soc.*, **30**, 291–298 (1953).
8. Francis, F., and Piper, S. H., *J. Am. Chem. Soc.*, **61**, 578 (1939).
9. Holde, D., in "Examination of Hydrocarbon Oils and Saponifiable Fats and Waxes," 2nd. ed. revised, edited by E. F. Mueller, New York, John Wiley & Sons, Inc., 1922.
10. Kissling, R., *Mat. grasses*, **3**, 1790–1801; 1837–1838 (1913).

11. Kitson, R. E., and Mitchell, L., Jr., *J., Ind. Eng. Chem., Anal. Ed.*, **21**, 401–403 (1949).
12. Koch, J. R., and Cocetta, Sister M., *Trans. Kentucky Acad. Sci.*, **13**, 104–110 (1950).
13. Lee, J. A., and Lowry, H. H., *Ind. Eng. Chem.*, **19**, 302–306 (1927).
14. Lewkowitsch, J., "Chemical Technology of Oils, Fats, and Waxes," 5th Ed., Vol. 1, p. 606, London, Macmillan & Co., Ltd., 1915.
15. Leys, Alex., *Ann. chim. anal.*, **17**, 334–342 (1912).
16. Lorenz, L., *Ann. Physik Chem.*, **11**, 70–103 (1880).
17. Lorentz, H. A., *Ann. Physik Chem.*, **9**, 641–665 (1880).
18. Luddy, F. E., Turner, A., Jr., and Scanlon, J. T., *Anal. Chem.*, **25**, 1497–1499 (1953).
19. Marcusson, J., *Chem. Rev. Fett- u. Harz-Ind.*, **15**, 193–195 (1908).
20. Marshall, A. W., *Anal. Chem.*, **22**, 842–844 (1950).
21. Meier, K., *Farbe u. Lack*, **57**, 437–439 (1951).
22. Menzies, A. W. C., *J. Am. Chem. Soc.*, **32**, 1624–1628 (1911).
23. Normann, W., *Chem. Rev. Fett- u. Harz-Ind.*, **19**, 205–206 (1912).
24. Ogg, C. L., *et al., Ind. Eng. Chem., Anal. Ed.*, **17**, 394–397 (1945).
25. Swietoslawski, W., "Ebulliometric Measurements," p. 172, New York Reinhold Publishing Corp., 1945.
26. Turner, W. R., Brown, D. S., and Harrison, D. V., *Ind. Eng. Chem.*, **47**, 1219–1228 (1955).
27. Wall, M. E., and Kelly, E. G., *Anal. Chem.*, **19**, 677–683 (1947).
28. Wand, M., *Chemist Analyst*, **28**, 3 (Nov. 1939).
29. Windaus, A., and Hauth, A., *Ber.*, **39**, 4378–4384 (1906); *ibid.*, **40**, 3681–3686 (1907).
30. Winkler, L. W., *Z. angew. Chem.*, **24**, 636–638 (1911).
31. Zöllner, W., *Farben, Lacke, Anstrichstoffe*, **3**, 385–390 (1949).

10. Wax Technology—Uses in Industry

Waxes are used in the arts and industries to the extent of hundreds of millions of pounds per year. Many different types of paper are waxed to wrap bread, cereals, cheese, and other foods. Paper containers for milk are waxed. Wax is used in preparing fruit and vegetables for the market. It is used as a coating for the liners that are inserted in closures for glass containers. In the brewing industry wax is used to line vats and barrels. Syrup barrels have wax linings. Cone-top cans for beer are lined with wax, as are certain similar containers used for packaging nonalcoholic beverages, whipped cream, etc.

Cosmetic creams have a wax base, as do rouge and lipstick. Wax is used in making crayons, in printing inks, in stoving varnishes, and in pencil and typewriter carbons. The use of wax in polishes of all kinds is extensive. Both the leather and rubber industries are important users of waxes. Almost all candles are made of wax. Wax is used for many electrical purposes, and in the manufacture of some explosives and pyrotechnics. There are many uses of wax in lubricants; it is used in antioxidants and pour-point depressants. Molding and casting techniques often involve the utilization of wax. It enters certain plastic compositions. Wax is indispensible in the manufacture of matches, and is of value in numerous handicrafts. Wax is used to some extent in sound records. The pharmaceutical industry is an extensive user of waxes.

In describing the use of wax in the arts and industries an alphabetical order of the latter is followed as closely as possible. In some instances the industries have been grouped for convenience, and therefore it may occasionally be necessary to consult the general index.

WAX IN ADHESIVES

The extensive use of waxes in adhesives has come about within recent years because of the availability of the microcrystalline waxes. Waxes are now being used as adhesives or adhesive adjuncts in numerous ways. In some instances wax is a component of wet glue where it is used as a lubricating or flexing agent. An important direct use of wax during the war periods was in the preparation of an adhesive layer between two webs of paper to form the laminated moistureproof wrapping material used to

package cigarettes—as a replacement for metal foil. The various functions of wax in the adhesive art may be summed up as follows:

(1) As a laminating adhesive, with or without the aid of other material, such as rubber, resin, etc.
(2) As a protective coating for wrapping which will by the aid of heat act as a "self-sealing" agent.
(3) As an ingredient of "hot melt" cements—useful in sticking dissimilar materials together.
(4) As an ingredient of the sticky surfacing agent for paper material, such as flypaper.
(5) As a lubricator in glues; and as flexing agent in adhesives.
(6) As a combining agent with rubber and resin for making adhesive-waxed tape, and masking tape.
(7) As an ingredient of a rubber-wax adhesive which can be applied by heat to the end of a shot cartridge.

Waxes are generally considered as adjuncts to adhesives rather than as adhesives, with the exception of *microcrystalline petroleum wax* of relatively high occluded oil content (7% or more). This latter type of wax is sticky at ordinary temperatures. Waxes that are to be combined with resin, rubber, or glue to produce adhesives need not necessarily be of a tacky nature. *Refined paraffin wax* possesses both cohesive and adhesive strength when its melt is chilled, and finds an extensive use in bread wraps where the wax provides a means of sealing the ends.

Wax as a Laminating Adhesive. Microcrystalline waxes recovered from petroleum tank bottoms or petrolatum, if not highly refined, contain 7 to 15 per cent of occluded oil, are quite sticky and remain so at ordinary cold temperatures. These waxes as first recovered usually are black in color. If partially bleached they are dark amber. Both the black and amber waxes find an extensive use in laminating. One of the well-known amber waxes is "Petrowax," a product of the Gulf Refining Company.

In using adhesive waxes to laminate paper to paper, or paper to foil, it is customary to spread molten wax on one web, and apply moisture to the other (if paper), and then to independently heat each web at about the same temperature, and join the heated webs together. The purpose of moistening the uncoated paper web is to prevent it from becoming too dry, to increase its stretch, and to prevent warpage of the finished laminated sheet. In this method the heated webs with the adhesive layer interposed are subjected to pressure after being "wed," and then chilled to set the adhesive. Suitable laminating apparatus has been designed for the industry, and consists essentially of a series of steam-heated and chilled rolls about which the paper is trailed.

A moisture-vapor resistant laminated film material is obtained when

films of cellophane or of "Pliofilm" (rubber hydrochloride) are bonded together by means of an adhesive comprising synthetic rubber, synthetic resin, and petroleum waxes. For example, 1,3-butadiene-styrene copolymer, 12 parts; coumarone-indene resin, 45 parts; a mixture of paraffin and microcrystalline waxes, 43 parts, and a solvent. [Carson, C. C., U. S. Patent 2,541,689 (1951)].

Wax Laminated Glassines. There are a number of wax laminated glassines used in packaging such as 57-pound "Wax Laminated Kleerview" of the Rhinelander Paper Company, Rhinelander, Wisconsin. This consists of two sheets of 25-pound per ream glassine laminated together with 7 pounds of wax. A similar laminated glassine of 62 pounds per ream is made of 25 pound per ream glassines with 12 pounds of wax between the sheets.

Other items are lacquered 54-pound and 58-pound wax laminated glassines, so-called 47-pound and 57-pound "Wax Laminated Kleerwraps;" 47-pound "Wax Laminated Snowdrift," which excludes light rays; and certain colored wax laminated glassines with amber, canary yellow, or other color. The amount of wax in the various wax laminated glassines usually ranges from 7 to 12 pounds per ream, depending upon the grade or quality desired.

Wax Laminated Metal Foils. Aluminum foil is laminated by the Reynolds Metals Company to paper tissue by means of wax to produce a laminate known as "Reyseal." "Reyseal" in turn can be laminated to chipboard, and the "Reyseal"-chipboard material convolutely wound to produce the body of a canister "Flex-Can" which has aluminum ends. The canisters are of value for packaging butter, jam, olive oil, motor oil, pharmaceuticals, etc.

Self-Sealing Wax Adhesive. A self-sealing wax adhesive may be of the thermoplastic or of the thermosetting type. A thermoplastic type is exemplified by the pressure-sensitive surface coating on masking tape; whereas the thermosetting type is met with in the wax composition used in bread wraps. In bread and cake wraps there are encountered problems concerning the rapidity of the setting and the sealing strength of the wax used. The addition of a very small amount of hard wax, such as *candelilla*, *"Castorwax," "A-C Polyethylene,"* or high melting point *microcrystalline wax*, tends to increase the sealing strength, and also give rigidity as well as gloss to the wrap. Because of the increased speed of modern bread-wrapping equipment an effort has been made to secure more positive and rapid self-sealing with the hot sealing irons. Some of the newer self-sealing bread wrap waxes contain 5 to 7½ per cent of *polyethylene*, 10 to 20 per cent microcrystalline wax (180/190°F) (ASTM), and 75 to 85 per cent paraffin (130/132°F) (ASTM); others contain "S-polymer-microcrystalline" wax blends added to the paraffin wax (see p. 509).

A "hot melt" coating of ethyl cellulose, colophony, and wax suitably combined may be applied to glassine or other cellulosic material for the purpose of rendering the package both moistureproof and self-sealing. Wraps of this sort have been used in packaging solid foods, including dehydrated material, for extensive shelf life. The use of an elastomer resin with paraffin wax (133/135°F) (ASTM) is sometimes resorted to in wraps for frozen food; e.g., 5 per cent of "Arwax" (34% polybutene) is added to the paraffin wax or "paraffin-microcrystalline wax blend" to secure a rapid heat-sealing wax coated wrap of parchment or glassine, and to enhance the moistureproofness of the wrapper.

A self-sealing wrapping paper can be made by coating one side of a thin, flexible paper sheet with unvulcanized rubber latex and the other with wax. The latex coating is dry and nontacky but self-adherent. The wax coating imparts moistureproofness. [Munising Paper Co., British Patent 666,501 (1952)].

A wax composition for the impregnation and coating of fibrous products, such as textiles, leather, wood, and in particular paper, for the use of wrapping foodstuffs, may be prepared by adding a prescribed amount of an *alkylated polystyrene* to a hydrocarbon wax. The polystyrene is alkylated with a polymerized propylene (preferably trimer, b.p. 175–225°C), and the product which has a molecular weight of 60,000 or more is mixed thoroughly with the wax, which may be a petroleum wax, ceresin, or ozocerite. [Butler, J. M. (to Monsanto Chemical Co.) U. S. Patent 2,580,996 (1952)].

Nonsolvent Adhesive. An adhesive for bonding cellular glass or other brittle, insulative materials has been proposed by Johnson. It consists of asphalt 4 to 6 parts, coumarone-indene resin 4 to 6 parts, *microcrystalline wax* 1 to 1.5 parts, and *chlorinated paraffin wax* (40%) 2 to 7 parts. The adhesive is characterized by masticity, vapor tightness, and resistance to cold flow. [Johnson, R. A., U. S. Patent 2,597,996 (1952)].

Hot Melt Cements. The name "hot melt cement" is given in the trade to a solvent-free cement which requires heating to make it fluid, and cooling to make it congeal and stick. Hot melt cements are used to stick paper to metal, paper to plastic, metal to glass, etc. Adhesives of the hot melt type may vary in consistency from a sticky flypaper adhesive to a fairly hard solid which will only become tacky when melted. Adhesives of the hot melt type, such as those made of asphaltum pitch or the like, do not always contain wax, but many of them do.

Some of the resins used in formulating hot melt cements are manila copal, processed congo copal, damar gum, methacrylate polymers, coumarone-indene, crude polystyrene, and other synthetics. Vegetable oils used with the resins may be boiled linseed, tung, peanut, castor, etc. Either refined *paraffines* or *microcrystalline petroleum waxes* are the most likely wax

constituents, although there are many special formulae in which *beeswax*, *shellac wax*, or a *vegetable wax* comprises the basic wax constituent. Natural crepe rubber and butyl rubber are also constituents in some cements, where low viscosity of the hot melt is not an important requirement. Polybutene, or S-polymer (polyethylene with polybutene), is a useful constituent in hot melt cements.

Sticky Flypaper. In the manufacture of sticky flypaper the paper web passes over a hot plate, or a series of hot rolls, to dry out latent moisture, and then through rolls which apply the adhesive on one side. By arranging the apparatus so that two of these coated webs face on the adhesive side, the paper can be rewound, cut to size, and the two webs pulled apart when ready for use in the household. Knoepfler[101] has given a composition for coating flypaper which is made by heating together linseed oil 7½, castor oil 7½, *beeswax* 3½, and rosin 36 parts. *Paraffin wax* and *ceresin wax* are also used in some formulas for sticky flypaper coating.

Wax as a Lubricator in Glues. Glues are improved in flexibility by the addition of a small amount of wax. The use of more than one per cent of a dry wax can destroy the adhesiveness of a wet glue. Hence the proportion of wax, such as ceresin, that can be advantageously added to a glue melt in water is about ½ to 100 parts of dry glue. In the manufacture of composition cork gaskets and gun wads the addition of a small amount of wax to the glue melt will facilitate the removal of the glue composited object from the metal mold which forms it. The wax can be used with animal glues, hide, or casein, or with vegetable glues such as mazein and soya. The wax-containing glue is spread over the granulated cork, while the glue is hot, and after chilling the cork composition is packed in the mold; it is heated again to soften the glue and cause the adhesively coated particles to adhere to one another. This is followed by a chilling of the mold in order to finish the composition article and eject it from the mold. The presence of wax in the composition obviates the necessity of lubricating the interior of the molds prior to the packing operation. Industrially the whole process is made automatic and continuous by the use of equipment designed for the purpose. The term glue as used above is in the broad sense as it may have a polyhydric alcohol, a waterproofing agent, or other material added to it besides the wax.

Burgundy pitch, Venice turpentine, or low polymerized synthetic resins are sometimes used in combination with wax to mount metallic foils on felt, composition cork, etc. in the manufacture of liners for closures used in sealing glass bottles or jars, and open-mouth cans.

Adhesive-Waxed Tape. Adhesive-waxed tape is paper or foil coated with a wax composition which will become adhesive when subjected to heat and pressure. It differs from a masking tape which requires only pressure to

apply it to another surface. Adhesive-wax tape may be also of such a nature that adhesiveness in its application to packaging is obtained through the use of a solvent to soften and activate the adhesion. These adhesively coated tapes, whether heat-sensitive or solvent-sensitive, have a wide use. The same principle applies to labels, sealing tape, papers for packaging, bottle-cap liner facings, initials or designs on fabrics, etc. In general, the heat-sensitive adhesives must not be too sensitive to climatic heats; otherwise the tape or foil would "block" in layers so that it could not be unwound from the spool.

Adhesive compositions suited to the coating of the tape or foil described above had been given by Kallander and Asnes[97] and have been used commercially. They employ wax, rubber, rubber antioxidant, zinc oxide, resin, and solvent, which must be mixed in a prescribed way. A solution of the rubber, in which has been milled the antioxidant, and zinc oxide, may be made with benzene, and then added to a benzene solution of the wax, together with naphtha, after which the solution of resin is added, with a small amount of alcohol. The wax may be *paraffin*, *anhydrous lanolin*, or other ester wax, depending on the use of the tape. A polymerized terpene resin is commonly used. *Vinyl acetate resin* can be used in some formulations. The rubber may be natural crepe, balata, or a synthetic elastomer. The compounding is carried out in a jacketed kettle, kept at a temperature of about 105°F. Rope paper is suitable for coating with such adhesives in the preparation of adhesive tape.

Masking Tape. A pressure-sensitive composition suitable for use on masking tape, tabs, posters, and similar articles, can be prepared from rubber, resins, *microcrystalline petroleum wax*, and mineral oil, or similar combinations in which wax is an ingredient. It is desirable to prepare a masking tape which can be attached to any surface by merely pressing the tape to the surface, and from which it can be readily removed without fouling or marring same. Abrams and Forcey[3] have given the following recipe for a peelable composition: rubber 30 parts, coumarone-indene resin (m. 40°C) 24 parts, coumarone-indene resin (m. 10°C) 28 parts, microcrystalline wax (m. 155°C) 15 parts, white mineral oil 2 parts, and hydroquinone 1 part. The resin acts as an adhesive agent, the rubber as a cohesive agent, the wax as a modifier, and the hydroquinone as an antioxidant.

According to Abrams and Forcey[3] a composition suitable for application to a paper base for use as removable units, tabs, or tape, may be made from: rubber 15, polybutene ("Vistanex") 15, *microcrystalline wax* 19, methyl abietate 25, ester gum 25, and hydroquinone 1 part by weight. Glycerol may be added to the composition to facilitate clean peeling. The composition is applied to the base sheet by means of a heated doctor roll or blade and in a thin layer. The finished tab or tape may be applied to

leather, textiles, paper, cardboard, bristol board, or to sheet material made of resins, viscose, cellulose acetate, regenerated cellulose and any other types of films.

Showcard Transparencies. Showcards, boards, fabrics, etc., can be furnished with a transparent foil or cellulose acetate by applying the latter to the entire surface with an adhesive composed of crepe rubber, burgundy pitch, and woolwax. The adhesive is prepared by adding a solution of 8 parts of crepe rubber dissolved in twice the quantity of petrolic ether to a preparation formed by melting together 8 parts of burgundy pitch and 4 parts of *woolwax* (anhydrous lanolin); 4 parts of petrolic ether are added after cooling. This adhesive is covered by a British patent granted to Beiersdorf Ltd., and Moore[13].

Horticultural Binding Tape. A corsage bouquet of orchards, or of cut flowers, can be effectively tied with a tape which has a composition of rubber and wax. The principle of the binding tape is that of admixing a thermoplastic body portion with a suitable binder portion homogeneously in order to render the tape flexible and stretchable. For example, according to Abrams and associates[2], a hardened solution of 18 per cent rubber and 72 per cent paraffin can be prepared for the purpose. The binding tape has appeared on the market in a green hue obviously to match the color of the flower stems.

Antiblock Wax Paper Coating. A wax paper coating composition may be prepared from *microcrystalline wax* 70 parts, *paraffin wax* 20–25 parts, and polyethylene (mol. wt. abt. 3000) 5 to 10 parts, the latter to prevent blocking. [Crown Zellerbach Corp. and Hyde, J. B., U. S. Patent 2,582,037 (1952)].

WAXES AS ANTIOXIDANTS AND POUR-POINT DEPRESSANTS

Wax as a Rust Preventative. Machinery, or machine parts, must often be protected from rust, particularly so when they are exposed to rain, snow, or sleet. They must be protected in overseas shipment through extreme changes in temperature and relative humidity. Aside from the numerous types of material that are used for wrapping machine parts, in many instances there is need for a protective coating applied directly to the metal. The surface coating must be either peelable or of such a nature that it can be washed off with an ordinary organic solvent such as gasoline.

Both petrolatums of special grades and anhydrous lanolin are customarily used for surface coating machine parts. Howe and Libby[86] proposed a rust preventative for use on metals which can be prepared from *petrolatum* 32, mineral oil 15, *anhydrous lanolin* 32, and mica 18 parts. They also stated that small amounts of cedar oil and graphite may be added. The purpose of the mineral oil is to thin the composition so that it may be readily ap-

plied to polished machinery by brush or otherwise. The lanolin and petrolatum make the coating cling to the metal. The mica makes the composition more compact, increases the coverage, increases resistance to the elements, and prevents the composition from rubbing off. The composition can be removed by using waste moistened with gasoline or kerosene.

H. E. Smith[164a] patented a peelable coating for machine parts. It is formulated from lanolin 8 to 20, polyethylmethacrylate 33 to 67, and fatty acid amide 33 to 44 parts. It is applied at 150°C and solidifies at 90°C.

Corrosion of the motor commutator or slip ring during periods when motors are idle can be prevented by the application of paraffin wax. When the motor is running the abrasive brushes will keep the copper parts free of corrosive films. Coating surfaces, by wax cake or stick, whenever a motor is not running will prevent corrosive action during nonuse periods. A suitable composition wax for stick use is one made up from *stearone* 50, and *paraffin wax* 50 parts.

Slushing Compounds. Slushing compounds of prescribed composition are used as protective coatings for exposed bright metals, or polished surfaces, to keep them from corroding. For example, Champion spark plugs are wax treated to arrest corrosion of the metal. The specifications of the U. S. Bureau of Standards for a "slushing oil" have been given by Walker and Steele[169] as follows: "The material shall firmly adhere to all metal surfaces at all temperatures to be met with under natural conditions and shall permanently remain in such condition that it may be readily removed by cotton waste wet with kerosene. On polished steel, iron, brass and copper surfaces at any temperature below 100° for not less than 5 days there shall be no stains or other evidence of corrosion." An oven salt-spray rain test is also specified and when time permits plates covered with the material should be exposed to weather test for 60 days with no appreciable rust in evidence as a result. Slushing oil leaves a soft film which can be easily removed at any time.

Wells'[172] composition consists of saponified lanolin dissolved in a hydrocarbon solvent. A thin film of the composition applied to tinplate used in the fabrication of bottle caps, cans, and the like will provide protection against corrosion during storage and shipment. The fatty acids or mixture of fatty acids and unsaponifiable matter of *woolwax* is also effective when made up in the same way with solvent.

Typical satisfactory formulas for protective coatings of the slushing type are (a) *candelilla wax* 3, rosin (grade H) 6, *petrolatum* (USP) 50 parts; and (b) *carnauba wax* 2, rosin (grade H) 5, and *petrolatum* (USP) 50 parts.

Types of Rust Preventatives. The Lion Oil Company, El Dorado, Kansas, produces an oil-type rust preventative of a lubricant-type in which the base oil in the preventative consists of an additive-type lubricating oil

containing a detergent and an antioxidant. To this base is added a sulfonate as a corrosion inhibitor, a metallic hydroxide, *oxidized paraffin wax*, and a water-displacing agent. The metallic hydroxide and oxidized paraffin wax are charged to a large soap mixer and saponified at 275 to 300°F for 2 to 3 hours. During this time the water-displacing agent and the sulfonate may be added. Small amounts of base oil are added, and when the minimum water content and desired saponification number are reached, sufficient additional oil is added to allow the mixture to be transported to the mixing tank where it is finished with the proper amount of lubricating oil.

The *semisolid-type compound* is made of lubricating oil distillate, *petrolatum*, and *microwax*, with or without water-displacing and rust-preventative agents. For the *solid-type compound* additional petrolatum and *microwax* are substituted for the lube distillate. The *hard base* "solvent-type" compound is an asphalt-base rust preventative, containing in addition to an asphalt (220–230°C softening point) a *metallic soap*, *microwax*, and a solvent such as naphtha.

The solvent type (hard base) of "Lion" rust preventative has a viscosity (SUS) of 350 seconds at 77°F, a flash (Pensky-Martens) 100°F, a specific gravity (API) 28°; it weighs 7.7 pounds to the gallon, is 55 per cent volatile, has semi-glassy black film characteristics, and dries in 60 minutes. It is applied by dip, spray, or brush, and lasts for two years on outside storage conditions. It is removable by petroleum solvents.

Refined mineral oil or paraffin compositions may be stabilized against oxidation, according to Moran *et al.*[119], by admixing a mere fraction of 1 per cent of an acetone dibenzyl mercaptol, or other mercaptol or mercaptal, which are organic sulfur-containing compounds.

All-Purpose Lubricating Grease. Lubricating grease containing petroleum sulfonates as rust inhibitors, and lithium stearate for heat stabilization, is marketed for all-purpose use. Butcosk[23] claims that the lithium salt of a petroleum sulfonate is also a new *rustproofing agent*. To prepare the grease a portion of a No. 57 viscosity oil is heated with free stearic acid to 160–180°F; lithium hydroxide dissolved in water is stirred in the oil; at 380–390°F more of the oil is added and the mixture adjusted to test neutral; and then a small amount of petroleum sulfonate is added. The grease is of an amber color, and unctuous, produces a translucent film, and is very resistant to water and heat.

Butcosk claims that a lubricating grease of the kind described regains its water repellency by the addition of metallic salts (Zn, Cd, or Mg) of 12-hydroxystearic acid. For example, a very water repellent grease can be produced when using the following formula: No. 57 viscosity oil 80, lithium stearate 16, petroleum sulfonate (mol. wt. 300 to 500) 2, and zinc hydroxystearate 2 parts. The finished composition is poured into shallow pans.

Specifications on a typical grease of this kind involve limits as to water absorption, melting point, leakage evaporation, starting and running torques at 0°C, corrosion resistance to salt spray, and several other tests.

Antioxidant for Lubricating Oil. For the elimination of carbonized sludge formed by oils operating at a high temperature, e.g. 500°F, over a period of time, Joseph Cole[33] of Whiting, Indiana, prepared an antioxidant composition with a base of *chlorinated paraffin wax* (43 per cent Cl) to add to the lubricating oil. The antioxidant is a compound of the wax 250 parts, oleic acid 250 parts, and anhydrous aluminum chloride 15 parts, all heated to 550°F, with constant stirring. A reaction takes place in which hydrogen chloride is evolved during heating, whereupon lime (25 parts) is then added and the whole transferred to a still; under 10 mm vacuum, 80 per cent of the product may be taken off on distillation. This distilled product has a specific gravity of 34 API, and about 1 per cent is added to the oil.

Wax as a Pour-Point Depressant. Mineral oil additives acting as pour-point depressants and viscosity index (VI) improvers are widely used by refining companies in the manufacture of lubricants. The preparation of these additives generally involves chlorination of either aliphatic or aromatic hydrocarbons, and condensation with or without the subsequent elimination of chlorine from the end-product. Polymers of waxy olefins, with or without chemical condensation, with cyclic hydrocarbons, function as pour-point depressants and VI improvers.

According to Lieber,[107], saturated hydrocarbons may be converted to olefins (alkanes to alkenes), and then polymerized by means of strong acids, whence the wax modifier is recovered. In the Lieber process chlorine is blown through melted paraffin at a temperature of 150 to 300°F, preferably limiting the chlorination to 10 to 12 per cent. The chlorinated wax is then dechlorinated by heating it to a high temperature and permitting the hydrochloric acid to split off and escape. By keeping the temperature below about 700°F a mixture of olefins is produced, without breaking carbon-to-carbon bonds. The dechlorination is facilitated by heating at lower temperatures in the presence of a catalyst, such as anhydrous barium chloride or activated clay. The alkenes resulting from the dechlorination can then be polymerized continuously by stirring for a long period the liquid alkenes with either sulfuric acid or phosphoric acid, preferably 60 to 66 Bé sulfuric acid, or 85 per cent phosphoric acid. The reaction should take place below 250°F, and be properly controlled to prevent carbonization. The reaction takes several hours and after completion the acid is removed with sodium hydroxide. The hydrocarbon content is taken up with kerosene so that it may be separated from the acid sludge. The final step of purification is to distil off the solvent and recover the *wax modifier* from the distillation residue.

A polymer produced with sulfuric acid from waxy olefins in the absence

of aromatics has, according to Lieber[107], an API gravity of 22.3; a viscosity at 210°F of 293 Saybolt seconds, and at 100°F of 4262 seconds; a pour point of +45°F; and a Conradson carbon of 6.1 per cent. When 1 per cent of this material was added to a waxy oil which had an initial pour point of 30°F, he found it to be reduced to +5°F; 5 per cent of the same material added to the same oil reduced its pour point to −20°F.

In the process of Davis[42] the pour-point depressant is made as follows: Paraffin wax is melted and heated to about 200°F, then chlorine is bubbled through it until 12 to 14 per cent is absorbed. The chlorinated paraffin is condensed with naphthalene using aluminum chloride ($AlCl_3$) as a reactor, the free HCl being expelled in the heat reaction to produce the end product.

In the process of Reiff[140] the chlorinated paraffin is condensed with phenol also using $AlCl_3$ as the reactor, heating the reactants, and expelling the HCl. If 3 per cent of $AlCl_3$ is used and the temperature is raised to 350°F, the resultant product is a wax-substituted phenol. The pour-point depressant is then referred to as a pure *poly-wax-substituted phenol*.

Frolich[64] prepared a condensation product of the chloronaphthalene type by reacting chlorinated paraffin with naphthenic acid (see p. 541). The reaction product was then diluted with kerosene and neutralized by adding water and alcohol to hydrolyse the catalyst. The recovery of the wax modifier follows the method of Lieber. The product had a Saybolt viscosity of 990 seconds at 130°F, 186 seconds at 210°F; it had an acid value of 4.3 and a saponification value of 8.3. The yield was about 40.5 per cent of optimum. When 5 per cent of this product was added to a waxy oil having a pour point of 30°F, it was found the pour point was reduced to +5°F. By using 100 grams instead of 50 grams of the $AlCl_3$ with 100 cc of chlorinated paraffin and 100 grams of naphthenic acid, a similar but more effective product was obtained. It required 1 per cent to reduce the pour point from 30°F to 15°F while 5 per cent reduced the pour point of the same oil to −5°F.

In 1947 the Standard Oil Development Company took out a British patent[139] for a condensation product of a halogenated aliphatic material of high molecular weight with an aromatic compound, prepared in the presence of a halogenated solvent of low molecular weight. If extracted with certain solvents it gives a product with high VI and excellent pour-point-depressing properties. The solvent extraction may be carried out at a temperature of 150 to 250°F and can be either batch or continuous. The solvents employed may be selected from a class of esters, alcohols, ketones, phenols, amines, ethers, etc. The lower esters, such as ethyl acetate, are favored. In an example chlorinated paraffin wax is condensed with naphthalene; $AlCl_3$ is used as the catalyst and tetrachloroethane as the solvent. As a pour-point depressant from 0.1 to 10 per cent may be used, the larger

amounts being employed when it is also desired to improve the viscosity index.

Wax Phenol Depressants of Reiff. Reiff and his co-workers[140a] have prepared and evaluated so-called "wax phenols" to be used for depressing the pour point of lubricating oils and also improving their viscosity, and as intermediates for the manufacture of resins, rubber substitutes, etc.

Condensation with an aliphatic carboxylic acid (e.g., oleic acid) of alkylated aromatic hydrocarbons or phenols (containing at least 20 carbon atoms in the side chain) gives carboxylic acids which are useful for such purposes. The alkyl-substituted hydroxy compounds can be prepared by the reaction of a chlorinated paraffin wax with a phenol, hence the name "wax phenol."

A wax phenol, according to Reiff, may be designated as "wax phenol *A-B*," where *A* is the number of atomic proportions of Cl in the chlorinated wax which reacted with the phenol, and *B* is the chlorine content of the "wax phenol." Wax phenol (3–16) 1 mol and oleic acid 1 mol are added to $AlCl_3$ 1 mol at 150°F, the mixture kept at 250°F for 2 hours, the product washed with dilute HCl and water, free from oleic acid by superheated steam at 390°F, and the resultant wax *hydroxyphenylstearic acid* (3–16) dried. For the preparation of a number of alkyl-substituted aromatic-aliphatic carboxylic acids, see U. S. Patent 2,475,916.

WAX IN THE BREWING INDUSTRY

The fermenting, ruh, finishing, and storage tanks in breweries are coated with wax-containing compounds. The composition of the protective wax compound varies somewhat with the material—wood, steel, or concrete—of which the tank is constructed. The wax compound is heated to 260–350°F for application by means of a propane torch and brush to the dry and heated surface of the tank. Many of such vessels require relining after periods of use; the linings are durable but not permanent. This relining is done by trained artisans. The coating material used for relining contains waxes like *paraffin*, *ceresin*, *ozocerite*, *montan crude* and *refined*, and the darker *microcrystalline waxes*.

Receptacles of large capacity in which malted liquors are customarily transported in the trade are barrels or kegs made of wood, or of metal, such as steel, aluminum, or stainless steel. In order to prevent the adsorption of impurities from such a receptacle into the beer or ale it has been customary to provide a lining to the receptacle. This lining is commonly referred to in the brewing trade as "pitch," irrespective of the exact nature of the composition. Brewer's pitch in a broad sense may then be defined as any pitch or pitch-like material suited for use in lining barrels. A pitch should have a slightly pine-like odor; it must contract and expand to the same extent as

wood, and have a melting point low enough for easy and fast removal of the old pitch when the barrels are to be repitched. Burgundy pitches of standard viscosity are commonly used, but there is also a demand for wax-coating composition type pitches.

Wax is used in lining cone-top beer cans to the extent of 3,000,000 pounds per annum. The total amount of waxes used in the brewing industry excluding purchased containers is estimated as approaching 1,000,000 pounds per annum.

Colophony Pitch for Brewers. The simplest or cheapest form of brewer's pitch for lining wooden barrels is a preparation consisting entirely of colophony. Colophony is the residue of rosin after the turpentine has been distilled off. However, better lining compounds are the so-called Burgundy pitches which are distilled cuts from rosin, lighter in color, more piney, and more lasting. It is necessary to line wooden barrels or kegs in order to preserve the wood from decay, and to provide an extremely smooth, cleansable surface for the inside of the keg to which impurities will not adhere.

Composition-type pitches of extra low viscosity for lining beer barrels made of wood or metal are marketed under trade names such as "Steramite Pitch" (John Eisenbeiss Corp.). In the handling of receptacles in the trade the interior lining is exposed to not only physical damage, but biological, and it is essential and customary not only to cleanse the "returned empties" to remove the sour dregs, but frequently to repitch them so as to have a container without interior imperfections. Pitching must be conducted with a material of 130° to 140°F melting point, one which will then permit of the employment of a pitching temperature below 200°F, for if the latter application temperature is exceeded the beer will develop a bitter taste. Examples of satisfactory rosin oil pitches are said to be: colophony 87, tasteless resin oil 8, and paraffin wax 5 parts; colophony 60, pine oil 30, resin oil 6, and paraffin wax 4 parts; rosin 78, resin oil 20, and wax 2 parts. Considerably less pitch is used for metal barrels than for wooden barrels (see Pitching Metal Barrels, p. 650). Olshausen and his associates[125a] have prescribed tests in detail for brewers pitch to include: odor and taste, viscosity, stability on heating, flexibility or elasticity, melting and softening points, ignition point, evaporation capacity at high temperature, presence of foreign matter, moisture, composition, and color.

Bituminous Pitch for Brewers. The native bitumens have many of the desirable properties of colophony, but are more tenacious and durable, and are more inert to both water and alcohol. The bitumens are to a great extent brittle and must be plasticized to make them useful.

A brewer's pitch may comprise a hard bitumen, free from mineral matter, and a suitable tempering agent comprised of wax tailings combined

with a petroleum pitch. Bitumens such as manjak (a hard bitumen found in the Islands of Barbadoes), gilsonite, grahamite, and wurtzilite are used.

In preparing brewer's pitch one or more of the hard bitumens are fused in a suitable vessel, and then a tempering agent such as wax tailings or wax from a still residuum is added in an amount sufficient to make the bitumen fluid enough to allow its application to the interior of the receptacle at a temperature between 150 and 200°C. The requirements are that the resultant pitch must not soften under summer heat, must be adhesive, and must present a smooth and glossy surface, which can be readily cleansed. The addition of colophony and rosin oil to the bitumen-wax composition imparts antiseptic properties and improves the spraying qualities of the pitch. In pitching large tanks the brewer's pitch may be dissolved in a solvent naphtha and applied by brushing.

A recipe for an improved brewer's pitch of the bitumen type was given in the letters patent granted to Forrest[62]. This recipe calls for 35 to 50 per cent of hard native bitumen (such as Barbadoes manjak, 15 to 25 per cent of wax tailings (petroleum wax or still wax), and 35 to 40 per cent of colophony and rosin oil mixture (1:1). The whole combination melts to a proper consistency for application at a moderate temperature, is easily sprayed, and provides the smooth, hard, durable, elastic, clean, and cleansable coating which is required. It is also mildly antiseptic, lacking any taste or odor, and is insoluble in alcohol or water.

Satisfactory results for keg lining are obtainable with brewer's pitch made from any one of the following combinations: (1) petroleum wax and gilsonite; (2) crude montan wax, and a natural pitch; (3) Aruba bitumen, ceresin wax, and kidney rosin oil. Aruba bitumen, also known as "Vanadiset resin," is produced from Venezuelan crude oil at the Lago Refinery, located on the island of Aruba, N.W.I. Generically the resin is the same as pitch on the one hand and asphalt on the other. The grades range from 149 to 204°C melting point. Kidney rosin oil is a rosin distillate and possesses an objectionable odor which the author finds can easily be eliminated by preheating before compounding. It is valuable as a tempering agent.

"Imported brewer's pitch" is the name given to a pitch that has been shipped in the past from Continental Europe to the United States, and was generally prepared from fully mature pine or other suitable forest tree by a process of heating the viscous exudation separated from its volatile constituent, until it became of suitable consistency and flash point. To this residue a certain proportion of rosin oil was added to give the pitch the necessary flexing property.

Evaluation of Brewer's Pitch. A first-class pitch for beer barrels should be as odorless and tasteless as possible, supple, of good consistency, stable to heating, of a high softening point, of high ignition point, and of low

evaporation capacity at high temperature. An acceptable pitch will have an ash content of 0.05 to 0.07 per cent, a specific gravity of about 1.0487 at 15.5°C, and a moisture content of less than 1 per cent; will be free from fatty and mineral acids; and contain less than 0.5 per cent of total impurities.

Stability on heating is determined by heating the pitch for 30 hours at 193°C (380°F), and then measuring the viscosity, which should not exceed 2.50 Engler degrees.

The usual method of determining the flexibility or elasticity is to dip thin strips of smooth red beech wood ($1\frac{1}{4} \times 8\frac{1}{2} \times \frac{1}{16}$ inches) into the melted pitch at 205°C (400°F); the strip is withdrawn and the film coating permitted to cool slowly to about 10°C (50°F). The strip when bent and broken should not crack or flake off, if the pitch is supple.

The softening or flow point is determined by the *A.S.T.M.* ring and ball method. An approximate melting point is obtained by the drop point method, or the *A.S.T.M.* cube method for tar pitches. The softening point should exceed 45°C (113°F) and the drop point 55°C (131°F), since the temperature of the water in the keg washer is sometimes over 40°C. If the softening point of the pitch is too high, the pitch will not penetrate sufficiently into the base material and is apt to crack.

Pitching Metal Barrels. Metal barrels are extensively used for packaging malted liquors. The barrels are of steel, stainless steel, or more often of aluminum. The colophony pitches so successfully used to line wooden barrels and kegs do not hold up well for metal containers. A satisfactory coating material may be prepared from colophony, bitumen, and 30 to 40 per cent of brown microcrystalline petroleum wax (m. 68 to 71°C). A pitch of this sort flows quite freely under heat, and can be applied at a somewhat lower temperature (105°C) than the colophony. The brown-colored microwax is used because it is cheaper than the yellow, and serves the purpose well. The wax pitches can also be used to advantage in lining large vessels of stainless steel. Plain steel barrels must be well coated with an asphaltic pitch, although they are seldom used. Stainless steel kegs are pitched only to add a favorable taste quality to the beer. At Monterrey, Mexico, pitch-lined half barrels of steel are pasteurized by the Luis Sada process, in a tray-type pasteurizer after racking. Marketing pasteurized beer in so large a container is unique.

Pitch for barrels should have a high melting point but a low viscosity. For example, a new half-barrel of wood construction may require 13 to 15 ounces of an ordinary pitch, but may be as effectively pitched with only 4 ounces when the pitch is of a wax composition of a low viscosity specification. Aluminum kegs require more flexible pitch than those of wood, or steel, since aluminum has a high coefficient of heat expansion. Compositions

for pitching kegs must be very fluid when melted, and therefore tank coating compounds, which are fused in small portions on the side wall of a tank, are not suitable for pitching.

Equipment for Pitching. The equipment used in pitching barrels and kegs can be classified as automatic, semiautomatic, or hand equipment. Fully automatic equipment from Neubecker a. Main is in operation in at least two breweries in the United States. This European system uses what is known as a "depitching pitch," with excellent solvent properties and fluidity, for removing the old lining from the returned empty keg. The keg is then moved to the pitching rack where it receives the new protective coating of pitch, the keg being drained and automatically revolved while heated to distribute the pitch clinging to the side walls. In this system a gas burner is not used for burning out the old pitch. Hence, "checking," leaks, blisters, and other defects are avoided when pitching solid oak or plywood barrels.

Other systems not as fully automatic are the Harnischfeege, and the Schlange. Systems known as the Essinger, and the Rauch are semiautomatic. In the Rauch system, for example, there is a preheater known as the Universal Preheater, which employs artificial or natural gas; a small flame is applied so that enough heat is available for the quick and thorough removal of the old pitch without having the flame touch the container. The keg while very hot is then placed on the pitching machine. Usually there are one or two nozzles, each handling a keg. The spray nozzle is umbrella-shaped and has about eighteen perforations which spread the pitch rapidly in a continuous stream to every part of the container, the excess pitch running into the well. The only moving machine part is a small inlet valve in each pitch kettle. There is an automatic control which times the operation in seconds. The air-spray pipe admits air through the pitch spray while the pitch is draining out, thus carrying off any smoke or vapor.

Wax Lining for Cans. Cans for packaging aqueous liquids, other than those to be subjected to high-temperature sterilization, may in some instances be lined to great advantage with wax. Such cans are made with a pouring spout or open mouth; the beer and carbonated beverage cans with a conical "crown-finish top." This top permits, in the course of manufacture, the entrance of a jet nozzle of a waxing machine by which means melted wax at a temperature approaching 200–210°F may be jetted into the can. The end having already been affixed to the can body, the wax at about 25 to 35°C above its melting point is jetted into the prewarmed container, by suitable automatic means. After waxing the inside of the can, the excess wax is allowed to drain. The can is usually made of lacquered or enamelled tin plate which also permits a better attachment of the wax than plain metal.

A wax used for lining beer cans must be free from taste and odor, of a melting point appreciably higher than that of pasteurization, of low viscosity, and supple at refrigerating temperature. The wax used for the purpose contains a considerable proportion of microcrystalline petroleum wax in its blend. The cans are generally filled to a 12 fluid ounce level and "crowned" at the brewery.

Cone top cans made for packaging nonalcoholic beverages are of 6 ounces, 12 ounces, or other suitable size. Some of the beverages, such as ginger ale, are highly carbonated. The wax used for such soft drink cans need not be of a very high melting point, but it must be extremely supple, and will necessarily have a relatively high penetration value. The wax used for the purpose contains a considerable proportion of microcrystalline.

According to Clayton, Johnson, and Sumner[31] wax can be deposited on the interior of a can by making the container the anode in an electrolytic deposition from an aqueous dispersion of wax. The dispersions are made of sodium silicate, sodium aluminate, or other suitable electrolyte. The wax used is beeswax, with paraffin, or ceresin, or a mixture containing a resin or a bitumen.

WAX CANDLES

Historical Development. The candle represents one of the most ancient and most useful forms of illumination. The candle is usually defined as a rod of fatty or waxy material through the center of which a fibrous wick extends. The excellence of a candle depends upon the nature of the wick and the combustible matter, and on the manner and extent to which these are apportioned. The prototype of the candle in the earliest days was most probably the *torch*, which must be regarded as a huge wick with the minimum amount of combustible matter, this proportion being altered until the ratio used at present, namely about one part wick to fifty parts of combustible material, was reached.

The development of the candle to its present form is one covering a period of many centuries. It is believed that earliest man used a *torch* made of pine branches or slips saturated with resinous or fatty matter. Then came the *link* made of rope strands steeped in rosin, tar, or pitch—or still earlier in asphaltum or bitumen. The link was followed by the *flambeau*, consisting of a core of hemp, soaked in rosin and coated with crude beeswax. According to Pliny, candles made of flax thread coated with wax and pitch were used by both Greeks and Romans for illumination in the first century A.D. In the Middle Ages the outer coat was made of bleached wax.

The *dip*, which is the name for a tallow candle, is probably derived from the *rush light*. The latter had a wick of rush-pith, later of crude flax or cot-

ton, and subsequently of twisted cotton yarn, coated with beeswax or tallow by repeated dippings; a counterpart is to be found in the *bougie* of continental Europe. The Christian era created a tremendous demand for beeswax candles for religious services, while the household candle was made of tallow. Finally came the *molds*, which were candles introduced about the 15th century by the Sieur de Brez. In these molds the hard tallow, spermaceti, or at a later date, paraffin wax, was cast around the wick of the mold. Varieties of molds are *rolled*, *poured*, and *drawn candles*.

Paraffin wax was not introduced in candlemaking until 1854. The bulk of modern candles are made of paraffin wax, or of *stearine*, or mixtures of these. Most of the beeswax candles made are for church use. The candlemaking materials are generally considered as "candle grease," stearine (stearic acid), paraffin wax, ceresin wax, montan wax, spermaceti, and beeswax.

The candle industry in the United States consumed an estimated 54 million pounds of waxes in 1951. Of this amount 50 million pounds was in *petroleum waxes*.

Dipped Candles. The making of *tallow dips*, which replaced the earlier rush lights, was conducted by alternate dipping and cooling of flax inkle in tallow, and was for centuries a household industry. In Paris during the 13th century a guild of traveling candlemakers went from house to house making candles. Tallow dips are still made today by numerous dippings of a plaited cotton wick. Tallow dips are used by plumbers as a flux.

Nondrip hand-dipped candles of the decorative type are made by either one of the following procedures.

(a) *Pouring method*. The wicks lengths are fastened to a holder usually circular like a hoop with the wicks evenly spaced around the circumference. The holder is suspended over the container of melted candle material so that it is free to turn. The molten mixture is taken up in a dipper and poured down the wick to accumulate on it. In this practice, the temperature of the wax is regulated so that it will flow down evenly and freely, but not drain excessively. After six to eight pours the candles are thoroughly cooled to obtain an adequate build-up with the subsequent pourings.

(b) *Dipping method*. The wick from a spool of wicking is wound back and forth on a thin rectangular metal frame to which is affixed a removable 3½ inch wide top plate with upturned flange having slots to hold the wick taut and in place. The frame, 9½ inch size, is dipped in the melted candle material, and after the wax has congealed, it is dipped again and again thoroughly cooling after six to eight dippings. After fourteen to fifteen dippings the wax builds up to about ⅜ inch thickness. The pairs of candles are now in V shape and are cut apart where they converge at the lower end

of the frame. The frame with candles now dangling is then dipped and redipped about twenty times more, or until the lower base of the candle is about 7/8 inch in thickness. Candles are removed from frame, butt ends removed, and given a final hand dip, and the end shaped with a fluted iron mold kept hot on a hot plate.

A nondrip candle composition for the first dips usually consists of 5 to 10 per cent *stearic acid*, and the remainder *paraffin*. After two-thirds of the candle material is deposited the remaining dips are in a mixture containing 20 to 30 per cent stearic acid and this is used until the candle is complete. When this type of candle is burned, the inner portion melts much more rapidly than the outer rim, thus forming a cup that holds the liquid fuel until it is burned.

Bayberry scented, dripless candles, hand-dipped 35 times, made in solid grayish-green color, are produced by Colonial Craftsmen, at Cape May Country Store, Cape May, New Jersey. Similar candles are made in New England and elsewhere. Hand-dipped candles are also made in various colors, associated with the perfume essences which are added to the wax such as rose, jasmine, gardenia, and sandalwood. Composition of waxes used in candlemaking are jealously guarded by candlemakers. Materials that are used include *bayberry wax*, *beeswax*, *paraffin* (136–138°F m.p.), microcrystalline petroleum wax, and stearic acid. "Decorative tapers" are made with about fifteen dips and similarly colored and scented.

The dipping process is also employed by larger manufacturers for the production of household and decorated candles. Hoop frames with wick lengths at regular spacings are repeatedly dipped into the molten candle composition to build up the candle to the required thickness. Several frames are attached to arms successively positioned over two or more of the containers of the candle composition, so that one operator can dip several frames at a time. The frames are counterbalanced to permit easier dipping and may even be moved up and down mechanically, although the mechanized procedure still requires the skill of the craftsman, for the temperature of the bath is critical in determining the flow of each new dip.

Dipped candles may be polished mechanically after final hardening by passing them through felt-covered rolls. If the candle is air-cooled a satin-like finish is obtained; if the freshly dipped candle is dipped into cold water a glossy or glazed surface results.

Spermaceti candles, which came into use in the latter half of the 18th century, are made in a similar manner. Spermaceti is used with some beeswax added to prevent brittleness in making the candle. For the standard sperm candle used in making laboratory measurements of candle power, not less than 3 or more than 4½ per cent of beeswax is permitted. The best air-bleached beeswax of about 144°F melting point must be used.

Source of the light	Power of the Light: Hefner Candles	Hourly Consumption of Fuel: In the Total	Hourly Consumption of Fuel: For 1 Hefner Candle	Hourly Amount of Evolved Heat (kilo calories): In the Total	Hourly Amount of Evolved Heat (kilo calories): For 1 Hefner Candle
Spermaceti candle	1.00	6.90 g	6.90 g	65	65
Stearin candle	1.09	8.58 g	7.87 g	78	69
Paraffin candle	1.35	8.47 g	6.27 g	87	64
Composition candle	1.25	8.54 g	6.94 g	81	66
Kerosene lamp	13.20	43.6 g	3.30 g	342	36.4

Taken from an illumination table of G. Lockermann [*Z. angew. Chem.*, **19**, 1763 (1906)].

Tapers are made by drawing long strands of slightly twisted cotton yarn repeatedly through a bath of molten wax. The tapers are cut to lengths, the ends dipped in hot water, and shaken. This process, called feathering, removes the wax from one end, and thus allows a new taper to be lit easily without dripping wax. *Tapers* are used for lighting Christmas trees and festive cakes. *Tapers* are referred to by the chandler as *drawn candles*. *Lighting-wicks* are made in a similar way to tapers.

Formerly, the larger church candles were made by rolling a big cake of warm wax, kneaded until it was plastic, around a wick. Then, by means of a rolling pin, the necessary smooth, uniform finish was imparted to the candle. The process has now been superseded by that of pouring. However, poured candles are likewise rolled to secure the desired finish.

Rolled Candles. Beeswax and ceresin are waxes that do not lend themselves to molding. Beeswax candles such as thick, long altar candles cannot be well made by the dipping or molding processes, since beeswax contracts much on cooling and has a tendency to stick to the mold. To make the candle properly the melted wax must be poured over the wick until after successive coolings the required thickness is obtained. The poured candle is rolled between two boards and then on a marble slab to give it the desired finish. Candles made from the microcrystalline petroleum waxes cannot be readily molded. Like beeswax, such waxes can be formed into strong pliable sheets, that is, by expressing from a suitable die under pressure, as described by Rau[137a]. The sheet material is then rolled into candles.

Highly Ornamental and Perfumed Candles. Highly ornamental candles, highly perfumed, appear to have had their origin in Persia (Iran) many centuries ago. It is told that one family of candle craftsmen in Iran was highly adept in the art of secret perfumes, incenses, fragrant oils, and waxes. The secret of their formulations was handed down for generations, and such candles were used only for banquets, weddings, and special occasions.

Two thousand years ago the Egyptians used waxes in painting. However,

the art of painting flowers on candles with handsomely colored waxes such as beeswax originated in America, exemplified by the ornamental perfumed bendproof candles of the Lapal Studios, Chalfont, Pennsylvania. Sizes most popular include 5-inch hurricanes, 10, 12, 15, 18, and 30 inch; the latter are banquet or studio candles. These are made to order in special designs of any hue; the paintings are in waxes which burn well and are scented with perfume.

Wedding and anniversary candles are painted with gold or pure silver that does not tarnish. Christmas candles are white with green holly leaves and red berries; red or blue mistletoe; bayberry, plain or decorated with holly and bayberry design. Baby gifts comprise 5-inch pink or blue candles with bunny and forget-me-not decorations. Painting of the tinted waxes is done by means of a brush, which is dipped in the molten wax. The candles have a fluted base, and are made of waxes that will not bend in the summer heat of the home. A 10-inch candle will withstand a temperature of 130°F without bending. Paraffin wax of 150°F melting point is generally used in their composition.

Ornamental candles in which the colored wax is applied by pallet blade or which are hand molded follow the craftsman's art which belonged to the creations of Florence, Venice, Rome, or the Orient, exemplified by the smooth shapes, hand rolled or hand twisted, produced by Antonio Ajello & Bros., candle craftsmen of New York. A handmade candle of distinction will combine color, form, and perfume, and will prove serviceable as well as ornamental. Highly ornamental candles are made of wax stained with suitable dyes in every hue and decorated with transfers or handwork. Candles are made with scents of honeysuckle, orange blossom, etc., and in antique, French twist, tree, or character shapes. Candles of this sort are made of dripless and long-burning waxes, and have a standard corrugated base to fit the candle holder. A pine tree shaped candle for yuletide is made from *bayberry wax* which emits a pleasant odor. [Also see Hand-dipped Candles, p. 654].

Molded Candles. In the modern use of the term "mold" we refer to a candle which has been manufactured by a molding machine. The machine for producing white household molded candles has several series of tubular molds in the center, wick spools below, and ejecting clamps above. The tubular molds are slightly tapered to facilitate ejection of the candles, and are fixed in a tank to which steam or water can be admitted. The lower ends are closed by the tip-molds which are carried each on a hollow piston rod. The piston rods are connected to a common bedplate. The upper or butt-ends open into a shallow trough. The clamps in the upper part of the machine are to hold the candles when ejected from the molds. Each mold has a spool of wick contained in a box under the machine. The molds are made of

Courtesy Muench-Kreuzer Candle Co., Inc., Syracuse, N. Y.
FIGURE 31. "Emkay" pillar candles, height 12 inches.

pure tin and the inner surfaces polished. The wick is threaded through the piston, through a perforation in the center of the tip-mold. The wick passes up through the mold and is held centrally by the candle last ejected into the clamp. The first step in the process of molding the candle is to pour the wax into the molds, which have been preheated to the proper temperature, leaving excess of wax in the trough. The candles are then cooled by filling the tank with cold water. The wicks are cut at the top and the clamps emptied. After the surplus wax in the trough has been scraped out, the bedplate is screwed up, and the candles ejected into the clamps.

As a paraffin candle tends to bend, it is necessary to stiffen it in one of several ways: by the addition of *stearine*, of *hydroxystearic acid*, or of a very high melting point *paraffin*. *Ceresin* is used for the same purpose. To give the paraffin candle oxygen-forming material as well as stiffness, 5 to 15 per cent of stearine may be added and it is then referred to as a "composition candle." In hot climates the stearine is considerably increased in the composition, or the candles may be made entirely of stearine.

Devotional Candles. Tallow dips are shipped from England to certain African tribes for their worship ceremonials. The Roman Catholic Church in its earliest period used beeswax exclusively for altar candles. These

candles were quite long and tapering, whereas those of the Greek Catholic Church were short and stocky. Today the Roman Catholic Church uses several types of candles of different composition. The two candles burning at the sides of the tabernacle on the altar, when Mass is said, are liturgically specified to contain over 50 per cent of beeswax. They are usually white in color, in contrast to the brown color of the Greek Orthodox Church candles, which are made from the crudest beeswax. Devotional candles other than those used on the altar are molded from suitable candle material and invariably dyed yellow. If of long shape, they are best made from a composition of the following order: *paraffin wax* 60, *stearic acid* 35, and *beeswax* 5 parts. The hydrogenated oils and fats serve as hardening agents for paraffin and are used chiefly for candles to be consumed in glasses, as in sanctuary lamps. A composition used for vigil-lights comprises *paraffin wax* 80 and *stearine* 20 parts. Vigil-lights are similar to the so-called night-lights. They are short, thick candles designed to burn 6 to 10 hours, formerly made of *coconut stearine*, but now usually of a low-melting paraffin wax. In Russia it was a common custom to sell the worshippers beeswax composition candles as a means of revenue to the church.

Votive lights are machine molded in much the same manner as candles, except they are made without wicks. In the molds there is a central metal pin, so that when the molded wax is ejected there is left a hole for subsequent wick insertion. The wick inserted is usually a low-melting metal wire wrapped with fine cotton yarn, and is supported by a tiny metal base to keep the wick erect as it burns. These lights give a very small flame.

Candle Material. For candlemaking ordinarily three grades of paraffin are used: (1) scale wax, (2) paraffin wax of 123–125°F melting point (ASTM), (3) paraffin wax of 128–130°F, or 133–135°F melting point (ASTM). The first item is used for glasses. The other items are blended with stearic acid to produce *household candles*. The addition of stearic acid to paraffin wax is for the purpose of hardening the candle composition, raising the bending point (softening point), and lowering the melting point. The change in melting point of the candle material is recorded by Geller[67]:

Candle Material		Melting Point (°F) ASTM
Paraffin 100%		125.6
plus stearic acid	2%	125.2
	10%	122.7
	14%	122.0
	20%	121.1
	25%	120.6

Household candles are made of paraffin alone, or of paraffin admixed with about 15 per cent of stearic acid. A *composite candle* may run as high as 30 per cent of stearic acid if made for shipment to warm climates. A so-called

stearine candle will have as high as 60–70 per cent stearic acid. *Birthday candles* are made of paraffin with little or no stearic acid added to the candle material.

The illuminating power of a candle is increased in proportion of the carbon content; the oxygen in stearine constitutes ballast and is of no significant value in illuminating power. Weight for weight, paraffin candles give almost one and a half times as much light as stearine candles.

Carnauba wax was used as a hardener for candle waxes one hundred years ago. English experimenters imported carnauba as early as 1911 for that purpose. Carnauba wax has, however, little value for increasing the bending point of a candle, and if more than 2 per cent is added to the candle material the candle will smoke, burn wet, and burn with too large a flame. *Montan wax* is only of value in giving the candle an opaque appearance, and its use is generally limited to 2 per cent. However, at Schliemann's factory in Hamburg a heavily bleached montan wax was combined with lignite paraffin for candlemaking. Waxes such as *beeswax* are sometimes refined for candlemaking, by heating the wax with $\frac{1}{10}$ per cent of an activated alkaline-earth mineral such as montmorillonite, preferably containing montronite and saponite, which have been activated by an acid (HCl) treatment. The mineral is added to the molten wax while the mixture is agitated mechanically and steam and air are passed through it. Beeswax candles are made in compositions of 51, 60, 75 per cent, etc. of beeswax, the balance paraffin wax. They are usually handmade but can be molded. The only use of resins in candlemaking is that of outside coatings.

Before the advent of hydrogenation in which oleic acid in commercial fatty acids can be converted to *stearine* for candlemaking, a cheap source of stearine was sought by converting oleic acid to stearic containing about 40 per cent of *hydroxystearic acid*. In 1905 the Standard Oil Company[157] was granted a letters patent in Germany for a candle composition of paraffine admixed with hydroxystearic-stearic acids. The latter was prepared in the following manner: The red oil (oleic acid) is dissolved in a 60 Bé petroleum distillate and treated with cold concentrated sulfuric acid, while maintaining the temperature of the reaction at 40°C. The sulfuric acid reacts with the oleic acid to form *stearolactone* (m. 51°C), and to a much greater extent, *sulfostearic acid*. The steam-heated mass is allowed to stand, and the acid water is drawn off below. The remaining mass is extracted with petroleum naphtha to dissolve the hydroxystearic acid, which separates out as a white mass on filtration, drying, and pressing. About 50 per cent of the oleic acid will have been converted. The by-product, stearolactone, and the unchanged oleic acid are then distilled to yield raw material for use in making the next batch. Hydroxystearic acid of this particular origin is probably a mixture of 9- and 10-hydroxystearic acids. It is recorded that the acid is

to be found in two forms, the *A* which melts at 77–85°C, and the *B* variety which melts at 81–85°C. For the purpose of facilitating its solution in *paraffin wax*, 3 parts of *hydroxystearic acid* are premixed with 1 part of the commercial *stearic acid*. Aside from the process described there are several other patented processes for converting monoethylenic acids into hydroxy monoethanoid acids.

Colored Candle Material. Cheap decorative candles are made by dipping molded white candles in colored hot wax. Inside the candle the composition is paraffin and a little stearic acid. The coating material is of paraffin but a little stearic acid is needed to dissolve the color. Brightness of color is accentuated by the softness of beeswax in combination with a little hard wax[67].

Candle material for colored candles is dyed in mass before molding when it is desired to produce finer quality candles. The stearine or composite wax is melted and an alcohol-soluble color stirred in; the amount of dye constitutes about 0.1 per cent by weight of the candle mass. For red it is customary to use Sudan IV, phloxine, rose Bengal, or rhodamine; for yellow, chinoline yellow, or auramine; for green, acid green, Victoria green, or chlorophyll; for blue, inulin, Victoria blue, or methyl violet. Monazo dyes are suited for coloring candle compositions.

Transparent candles for ornamental purposes may be made by adding to a paraffine melt about 2 per cent of β-naphthol; or by melting petrolatum in the candle material. Martin[113] has given the following recipes: (1) paraffin wax 70, stearine 15, petrolatum 15, for a low-melting, transparent candle; and (2) paraffin wax 90, stearin 5, petrolatum 5, for a higher melting, less transparent candle. β-naphthol candles burn with an objectionable odor.

Bending and Dripping Properties of Candles. The bending point is the temperature at which a candle softens and starts to bend. For this purpose the candle is tested by keeping it in a thermostatically controlled cabinet for about seven hours at constant temperature. The wax must, however, soften before it reaches the melting point. The difference between the softening point and melting point in candle material is of the order of 10 to 20°F. *Stearic acid* is ordinarily the best agent to increase the bending point of a candle composition.

Materials which have been used for the purpose of hardening and improving the dripping property of candles are (1) hard waxes such as *carnauba*, *montan*, *candelilla*, and very high melting hydrocarbons; (2) synthetic waxes such as certain *Gersthofen waxes*, *cetyl alcohol*, *Oxo molecular waxes*, *polyethylene wax*, etc.; (3) *stearic acid*, *palmitic acid*, fatty acid amides such as *stearamide*, etc., high molecular weight ketones, *-stearone*, *palmitone*, etc.; (4) hydrogenated oils and fats, like *Castorwax*. Aside from *stearic acid*, these materials have only specialty uses. The estimated con-

sumption of candelilla wax of 700,000 pounds as a candle-hardening material (*CW* Report, *Chemical Week*, Sept. 27, 1952) would appear to exceed that of all other hardening materials combined, excluding stearic acid.

For candle material used in glasses (at altar rails) the hydrogenated oil products when mixed with *scale wax* prove better than stearic acid. Candles consumed in glasses are 1¼ to 4 inches in diameter, and are low in height (½ to 7 inches).

Candle Wick Specifications. The plaited and pickled wick was first introduced in France in 1825. The early wicks, which were neither plaited nor pickled, did not bend over to the outer oxidizing region of the flame and consequently were not completely consumed; they required frequent snuffing to remove the char. Molding machines of a continuous wicking type were introduced in England in 1834. In modern machines 500 candles or more can be produced with one charge of the machine, and the output is two to three charges per hour per machine, in molded candles. In the United States the use of wax in the candle industry has grown to enormous proportion, namely estimated 54 million pounds, hence the demand for a tremendous yardage of wicking material.

The wick for a candle consists of a cotton yarn ranging from 4-9s to 20-26s count, which is flat braided by machinery from three groups of yarn made up of 3 to 12 or more strands with 7 to 12 plaits per inch. The finer the count of the yarn, the more strands per group and the greater the number of plaits per inch. Suck a wick, installed in a candle of given size and composition, provides a relative size flame and burning rate. The plaited wick material is supplied by the cotton spinner to the chandler who pickles it for use. It is boiled in a weak caustic soda solution, bleached with chlorine or hypochlorite, soured with dilute hydrochloric acid, and washed with clear water. The bleached plait is pickled with a solution of mineral salts, such as boric acid and niter, sal ammoniac, or other suitable chemical to help fuse the ash of the wick when the candle is burned and thus prevent smoking. One pickling formula is ammonium phosphate 7, ammonium sulfate 7, sodium borate 0.5, and water 1000 parts.[100a] The pickling treatment is applied to hanks of material several days before the wick is to be used. The wick plaits are steeped in the chemical solution for 24 hours, placed on a perforated shelf to drain, and then dried by means of a centrifugal machine. After drying the chemically treated wick is wound on spools for use.

Shapes and Sizes of Candles. Stearine or composition candles are sold in many shapes and sizes, and are classified as to the number per pound, the length, and the diameter. In 12-ounce candles we have "short shape," "long shape," or "tube." A short shape, for example, might be 4½ inches long and $^{13}/_{16}$ inches in diameter with 12 candles to the pound; a long shape

9 inches long, ¾ inches in diameter, with 8 candles to the pound. A tube candle would be a long shape but smaller in diameter with 12 candles to the pound. There are other shapes and sizes in 14-ounce candles. There are also "self-fitting candles," "cable toy" in assorted colors; "coach" which are 1⅛ or 1¼ inches in thickness; "night-lights" burning 8 to 10 hours; and "starlights." Candles are sold by the pound or box.

Molds in *beeswax* come in self-fitting or in plain ends. Tapering wax candles may be hollow or solid at the base. "Renaissance candles" are made in beeswax or *stearine*. Then there are the handmade patent-finish beeswax made in a number of lengths ranging from 9 to 22 inches. Easter or Paschal candles range from 32 to 64 inches in length and 1½ to 3½ inches in thickness. A 59-inch candle with 3½ inch diameter weighs 20 pounds.

Candles are also molded in prismatic cross sections such as square, triangular, octagonal, etc. Spirally fluted candles must be made to rotate when ejected from the mold. Large church candles are often channeled by longitudinal shafts so that the melted matter will flow into the interior of the candle instead of guttering on the outside. Melted candle stock is also crutched previous to casting so as to secure more candles per given weight of candle stock. Such candles are consumed rapidly.

There is a popular demand for ornamental figurines in white and colors, with a central wick; e.g., the "Tavern" novelty candles produced by the Socony Mobil Oil Company. They are made largely of *paraffin wax* in sectiona molds.

Disinfectant Candles. Paraform candles of 2 to 11 days' life are used for disinfecting the atmosphere in hospitals and in the home. They can be made from stearic acid 20 parts, paraffin wax 40 parts, and paraformaldehyde 20 parts. The stearic acid and paraffin are melted in a container with hot water or steam heat, and after thoroughly mixing and cooling to pouring consistency, the paraformaldehyde is stirred in rapidly as the wax is poured into water-cooled molds, to avoid loss by evaporation. Another composition which employs a 40 per cent solution of formaldehyde is as follows: paraformaldehyde 8, formaldehyde 5.5, *stearic acid* 16, and *paraffin wax* 16 parts.

Wind Torches. The torch as an example of man's earliest means of illumination has already been referred to. The modern torch instead of being made of pine branches saturated with resinous or fatty matter, is made from wax, pitch and rosin, or rosin alone. A *wind torch* of this kind is supplied with a handle and cup. When made of wax alone, three or four candles are grouped and soldered together to make a compound candle with several wicks.

A torch may be made by impregnating a chemically treated wick, such as one of twenty or more hemp threads saturated with a saltpetre solution

and dried, with equal parts of wax and Venice turpentine, thickened like candles by pouring, and finished by rolling; the candles are then grouped together by soldering. Or, a sharply dried hemp-wick of thumb thickness is saturated with equal parts of wax, raw turpentine, and tallow, and hung to dry. The wick is then thickened by pouring, rolled, cut, and grouped. According to Andes[8] these torches are cheap and effective; they will remain burning in storm and rain.

Chinese Candles. Candles are made in China from a vegetable tallow obtained from the seeds of *Stillingia sebifera* Willd. The seeds are about as large as hazel nuts, black in color, and are covered with a fairly hard layer of white tallow; the seed albumen also contains fat. The seeds are pounded in mortars, and exposed to steam for 15 minutes in cylindrical vessels, after which the mass is gently pressed. The congealed mass is warmed over hot embers and filtered through straw. Over 20,000 tons of this tallow are said to be produced in China each year. The tallow consists of *tripalmitin* and *oleodipalmitin*, accompanied with small amounts of the glycerides of lauric, myristric, and stearic acids.

Solidified Alcohol. There is a demand for a canned fuel that can be easily handled and transported for the heating of small quantities of material. Commercial products of this nature have appeared on the market as "Solidified Spirit," "Solid Spirit," "Alcohol Cubes," "Travellers' Alcohol," "Smaragdin," etc. They are prepared by adding to commercial ethyl alcohol a solidifying ingredient, and when the mixture solidifies sufficiently, it is cut into cubes of one inch diameter, or other forms suitable for the market.

An early Belgian process was to add to the alcohol a sodium soap charged with several times its weight of sodium silicate, warming same and then allowing the mass to solidify. Soap and *paraffin wax* have also been used in the same way. Such preparations either decrease the calorific power of the alcohol substantially, and cause it to burn slowly; or they impair free burning and leave quantities of unconsumed residue. Cellulose nitrate[181] will increase the rate of combustion.

In one form of preparation the alcohol is solidified by the addition of 5 to 15 per cent of *vegetable wax*, *stearine*, or *paraffin wax*, together with a sufficient amount of cellulose nitrate to impart the freedom of burning desired. In another preparation a synthetic tristearin, made from stearic acid and glycerin at a high temperature, is combined with a cellulose nitrate solution in such a proportion that the mass on cooling will separate out in a solid state. The temperature of mixing the tristearin and nitrocellulose should be maintained at 40°C. One formula calls for tristearin 3, sodium sebacate 5, nitrocellulose in solution 1, and alcohol 91 parts.

Solidified alcohol produced from the latter cellulose nitrate formulation

produces a flame with maximum heat, melts very slowly, leaves little residue, and obviates all danger of explosion. Cellulose acetate has also been used as the gelatinizing medium, and is said to keep the burning mass from excessive liquefaction. A small quantity of *stearic acid* adds greatly to the firmness of the product.

WAX IN CERAMICS

Ceramics as here implied relates to the study of the art of pottery, which includes all objects fashioned from clay and then hardened by fire, including porcelain which is a well marked variety of pottery. Whether wax was used in ancient ceramics is not known with certainty.

Historic Uses. Excavations of pottery produced in the Sung Dynasty (960–1279) have revealed that stoneware with gray or light buff body had been covered with a wash of "white slip" and bears a beautiful waxen glaze closely crackled, acquiring a beautiful pinkish-gray stain during burial. If wax was used as "glaze resist" possibly a native vegetable tallow might have been employed.

In the early 16th century at Seville and Toledo were produced polychrome-enameled tiles. The geometrical or other designs were outlined with color by painting these in manganese with a waxy medium. Earthenware dishes with bold animal designs were executed by the waxy color technique employed at Toledo. Even today hot wax is used to some extent as a carrier for ceramic stains. In ceramic manufacture *paraffin wax* is used for coating spots that are to be unglazed. *Beeswax* has been used as a resist in an acid-etching process for decorating ware.

Modern Uses. In modern times paraffin and *microcrystalline waxes*, especially in emulsion form, have been extensively used as (a) binders and lubricant in both bodies and glazes; (b) in acid etching; and (c) for underglazed "decal" work on dinnerware. Semivitreous ware is made by molding and baking the clay material at under-fusion temperature, in which state the ware is capable of absorbing water, or, the surface is rough enough so that the wax will hold onto it.

When cool the ware is painted with a microcrystalline wax-soap emulsion on the surface, to which the decalcomania is to be applied. Then after applying the "decal" the ware is placed in water to float off the paper. The next step is to spray or dip with the glaze, which consists of a water emulsion of silica or the like. Then the ware is fired for 18 to 24 hours at a high temperature, which causes the wax to burn out.

The microcrystalline wax emulsion contains as much as 50 per cent of solids, and the wax particles are 1 to 3 microns in size. "Ceramul 2305" of the Socony Mobil Oil Company is an emulsion of this type. In ceramic use only nonmetallic emulsifiers may be employed in a wax emulsion so that no ash or residue remains after firing.

Commercial *fatty acid amides* have proved valuable in providing adequate protection for fusible decorative coatings on ceramics and glassware. These decorations are applied by running a tumbler, ash tray, or other glass object under a heated wire screen printer. After coating, conveyors carry the printed ware to ovens where the decoration is permanently fused to the glass. The coating consists basically of a mixture of pigments, fine sand, and binder.

Normally care must be taken in handling the glassware before the fusing has taken place. However, the addition of a small amount of the amide (e.g., "Armid") to the mixture permits transporting freshly coated glassware to the ovens without danger of transferring or smearing the decoration on the conveyor line. At the oven the amide, rosin, and solvent volatilize, leaving the fine sand and pigments to fuse and form a permanent bond to the glass or ceramic surface.

Miscellaneous Uses. Unglazed flowerpots are sometimes waterproofed by treating the inside surface with a wax emulsion. Efflorescence in a brick wall can be arrested by the proper wax emulsion treatment. Van Horn[166] has described the value of wax in producing superior steatite dielectrics in which steatite can be used with but little clay. A combination of 3 per cent of water-soluble materials (gums, starches, lignin extracts, dextrin, and the like) and 3 per cent of high-melting *microcrystalline wax* provides a superior type of binder for the building of ceramic bodies with sufficient plastic flow to permit molding complex shapes without excessive forming processes. If a steatite body contains sufficient clay to provide plastic strength at the mixer a wax may be used as the only organic binder. The incorporation of a little fatty acid soap assists as an antisticking agent. Waxes in the presence of water act as lubricants, and are helpful in extrusion processes. "*Carbowax*" may be used as a binder for ceramic pigments.

WAX IN CHEWING GUMS

Chewing Gum Base. Chewing gum base is a compound of an elastomer, resin, and wax, to which other material can be added to produce chewing gum. The elastomer may consist of gum chicle, spruce gum, a selected balata, pontianak, jelutong, gum gutta, or a synthetic rubber-like compound such as polystyrene or butyl rubber. Natural and synthetic latexes are also used in place of solid elastomers, e.g., in bubble gum. Resins of various kind, natural and synthetic, are in use. The waxes employed by the converter are hard and of high melting point. *Candelilla wax* is commonly used, also fully refined hard block paraffin (e.g., 143/145°F or 148/150°F AMP); in fact any hard, edible wax with the requisite physical properties including *sugarcane wax*. The amount of wax which is used in a chewing gum base usually ranges between 5 and 10 per cent, inclusive of

2 per cent of block paraffin. About 3 million pounds of candelilla wax are consumed each year by the chewing gum industry.

Generally speaking, the rubber-like crudes must be broken down by milling before they can be made masticable for incorporation of wax, or wax and resin. For example, when chewing gum base is made from crude pontianak (jelutong) it is necessary to knead the material at 93 to 140°C until it becomes masticable. The pontianak resins, purified by treatment with alkali and sugar solutions, and with superheated steam, may be mixed with coconut oil or other softener, including *japanwax*, before incorporating the harder wax, such as *candelilla* or *beeswax* and later processing with the customary flavoring and sweetening ingredients.

To the chewing gum base, as above described, the chewing gum manufacturer adds powdered sugar, corn syrup, a little water, flavoring, fixative, and coloring to produce chewing gum. The finished gum contains 25 to 30 per cent of base, and 70 to 75 per cent of sugar, flavoring syrup, and starch. The mixing of the ingredients is done in a kettle at a temperature of 80°C (176°F) and takes about an hour, or until the moisture content of the finished batch is down to a predetermined level (8–9 per cent). From the mixing kettle the batch is transported by lift-truck to the cutter, which divides the batch into loaves of the proper size to feed to the extruder.

Carmody[26] proposed combining a synthetic resin with the elastomer, vegetable oil, and wax, making the synthetic resin the predominating masticable ingredient, as exemplified by a chewing gum base comprised of hydrogenated pinene resin 66, rubber elastomer 25, vegetable oil 5, and wax 4 parts. Cohoe[32a] patented a chewing gum base of elastomer and resin in which materials like butyl methacrylate, a methyl ester of hydrogenated abietic acid ("Hercolyn"), modified-terpene condensate, maleic modified rosin ester, and urea-formaldehyde resin are used; the plasticized butyl methacrylate resin in conjunction with *candelilla wax* comprises about 25 per cent of the composition. The gum base is made by mixing and heating the materials together, to be later compounded with suitable sugars and flavorings in the customary manner. The thermosetting resin imparts a structure to the base which makes it firm and rigid, but friable, and the gum becomes soft at mouth temperature. A small amount of urea milled into chewing gum composition is said to function as a bacteriostatic agent.

Bubble Gum. In the manufacture of bubble gum, in which latices of natural or synthetic rubber are used, the ingredients for each batch, 700 pounds more or less, are palletized in the preparation department. After weighing it is customary to place each ingredient on the pallet in the order in which it is to be incorporated in the product. From the mixing kettles batches are dumped by hydraulic lift into trucks and transported to cutters, which divide the batch into loaves for the extruders. The gum leaves the

extruder at 16 ropes of exact diameter, which are then guillotined into uniform lengths and delivered mechanically to trays, 32 ropes to the tray. The trays on the trucks are held in air conditioned rooms for cooling and tempering, then cut to "kiss" size and machine wrapped, as at the Paris Gum Corporation of America, McAllen, Texas.

The ingredients of bubble gum may comprise natural and/or synthetic latex, edible waxes such as *sugarcane wax*, resins, plasticizer, powdered sugar, flavor, corn syrup, and coloring. They are added one by one in the mixing operation, which requires an hour at a warm temperature.

WAX IN COSMETICS

Historical. Cosmetics are substances of diverse origin skillfully compounded to impart beauty to the person. They have one or more of the following functions to perform: (a) to cleanse, (b) to allay skin troubles, (c) to cover up imperfections, and (d) to beautify. They have been in use since the days of the early Egyptians. For example, beautifully carved unguent vases in alabaster displayed in the British Museum date back to 3500 B.C. The earliest cosmetics were probably vegetable oils and tallows of a crude nature but fragrant. The oils were sesame, almond, and olive. The cosmetics used later by the Romans, such as the solid unguents, were perfumed with almond, rose, or quince. It is possible that *beeswax* may have been one of the constituents.

Cosmetics were brought into Britain at the time of the Crusades. Cosmetics of all kinds were in great favor by the court of Louis XIII. The modern cosmetics that have a wax foundation include cleansing cream, greaseless cream, vanishing cream, skin cream, hormone cream, cold cream, unguent, lipstick, etc. They are simply refinements of many of the earliest cosmetics.

Wax Ingredients in Cosmetics. The waxy ingredients that enter into the making of cosmetics are *lanolin*, both hydrous and anhydrous; *white wax* (bleached beeswax); *cocoa butter*; *stearic acid*; and *microcrystalline waxes*; as well as plain *paraffin*, *ozokerite*, *spermaceti*, waxy alcohols (e.g., *cetyl* and *stearyl alcohols*), and a few others. In cleansing, vanishing, and greaseless creams, *stearic acid* with or without alkaline reagent plays an important role. The cosmetic industry is the largest user of *beeswax*. The alkaline reagents are principally sodium borate, potassium carbonate, and ammonia. Triethanolamine is the alkaline reagent that is sometimes used with stearic acid.

Although only a fourth of the cosmetics made in the United States contain wax or waxlike material, the volume of such cosmetics is estimated to exceed $45,000,000 in value per annum.

Emollients in Cosmetics. In recipes for cosmetics there is usually wax,

an emollient, distilled or deionized water, an alkaline reagent or emulsifying agent, and a perfume, for example, beeswax 1, grapeseed oil 3, water 2, and sodium borate 0.05 part. Cosmetics are prepared by emulsifying a wax in water by means of an emollient and an emulsifying agent. The addition of perfume lends attractiveness to the cosmetic. In this class of cosmetics are cold creams, emollient creams, cleansing creams, superfatted cleansing creams, absorption base creams, hand creams and lotions, foot creams, and baby creams and oils. There are a number of other cosmetics which are less dependent upon an emollient, such as cream shampoos, sunburn preparations, etc. Emollients are used for their local softening, soothing, relaxing, and protective actions. In preparing the cosmetic the procedure in general is to melt the wax and the emollient together, and then slowly add to the hot melt the aqueous solution containing the alkaline ingredient, stirring to obtain a creamy and permanent emulsion. An emollient must be chosen that is compatible with both the wax ingredient and the alkaline solution. Emulsifying agents are amino glycols, alkanolamines, esters of polyhydric alcohols, etc. The emollients used in cosmetics are almond oil, grapeseed oil, white mineral oil, glycerol, castor oil, cholesterol, anhydrous or hydrous lanolin, petrolatum, and others. Any of these may be readily combined with the wax and alkaline reagent. Stearic acid functions as a wax. For example, let us consider the recipe for a greaseless cold cream of the following order: *stearic acid* 14, glycerol 12, potassium carbonate 4, water 8, sodium borate 1 part, and perfume q.s. (a quantity sufficient). Without directions given with the recipe the logical procedure would be to melt the stearic acid in a kettle, with most of the water. The potassium carbonate and sodium borate would be dissolved in hot water, and added to the stearic acid and water; after thorough stirring, the mixture would be beaten so as to saponify the stearic acid. Some time would elapse before adding glycerol, and perhaps the mixture would require reheating, and then on cooling the perfume would be added.

Nonhydrocarbons used with emollients include *white* or *yellow beeswax*, *spermaceti*, *cetyl alcohol*, *stearyl alcohol*; hydrocarbon materials include *paraffin*, *ceresin*, *ozocerite*, and *microcrystalline waxes*. It is claimed that paraffins clog pores and cause them to become enlarged or infected. The nonhydrocarbon types of waxes are preferred in cosmetics.

Polyhydric alcohol fatty acid esters play an important role in cosmetic dermatology. *Glyceryl monostearate* is of particular value in the formulation of antiperspirant creams since it is nonionic in character and serves to permit the introduction of a large amount of electrolyte in the emulsion. It has been possible to prepare a stable cream containing as much as 20 per cent of aluminum sulfate by forming the emulsion with glyceryl monostearate in conjunction with other surface-active agents not affected by an acid pH.

Small additions of monoglycerides or of *sorbitan esters* enhance the stability of many of the hand lotions. Highly *ethoxylated sorbitan monolaurate* serves to disperse essential oils in water so as to make them appear to be in solution. *Glyceryl-monolaurate monosulfate* is used as a detergent in dentifrices.

Cold Cream. Cold cream is a soft, oily, cooling cosmetic, consisting mainly of an oil, water, beeswax, and mild alkali. The alkali is one that assists in producing a water-in-oil emulsion, sodium borate being selected for the purpose. It is of interest to note that cold cream originated with the French Pharmacopoeia, the so-called *Medicamentarius*, and that the French cold cream was virtually a rose-water ointment, after which "Rose Water Ointment, USP" has been patterned. English rose cold cream is of a similar order. It is prepared from liquid paraffin 61 parts, white beeswax 18 parts, rose water undiluted 20 parts, and sodium borate 1 part. Perfumes and pink color, if desired, are added in small amounts. The perfume consists of French rose geranium 70, patchouli 20, and essence of synthetic musk 10 parts. The color consists of a trace of alkanin or amaranth.

The United States Pharmacopoeia (USP) adopted the following recipe: (A) *Spermaceti* 125, *white wax* 120, expressed oil of almond 560 parts. The waxes are melted together on a water bath, the almond oil added, and heating continued until the temperature of the mixture has reached 70°C. (B) Sodium borate, 5 parts, is dissolved in distilled water, 140 parts, and rose water 50 parts, and the solution warmed to 70°C. (B) is gradually added to (A), and the mixture stirred rapidly and continuously until it has cooled to 45°C; then 0.2 part of rose oil is added. While this preparation is often called "cold cream," none of the cold creams, such as cleansing cold cream, resemble the official formula. The commercial cold creams, as a rule, are made with a liquid petrolatum base. High-grade bleached paraffin oil, patterned after what was known as Russian white mineral oil, does not develop rancidity as does almond oil, and is less expensive to use. A commercial recipe of cold cream is as follows: *white beeswax* 150, white paraffin oil 600, sodium borate 9, water 240, and perfume 1 part. The white wax is melted in the paraffin oil by gentle heating. The sodium borate is dissolved in warm water. The two fluids separately are brought to a uniform temperature not exceeding 60°C. The aqueous solution is poured into the oily one in a continuous stream, stirring gently for a minute or two. Then while stirring, 1 part of oil of geranium and a little oil of rose are added. Sodium borate in cold cream greatly assists as a whitening agent and as a stabilizer.

In commercial production, when a mechanical filler is not available, a glass-lined pot with a long spout may be used to pour the cold cream at about 40 to 42°C into the jars. The vessel in which the waxes are melted should be glass lined, and of stainless steel, aluminum, or other chemically

resistant metal. Heating is best done on an electrically controlled hot-plate. Paddles for stirring should be made of wood. Artificial vanillin is not recommended as a perfuming agent since the cold cream is apt to turn pink and later brown during its shelf-life.

Ceresin waxes have been used in making cleansing cold cream. A recipe is as follows: white mineral oil 15, *white beeswax* 2, pure *ozocerite* 1, *white ceresin* 2, water 8.3, sodium borate 0.2, and perfume 0.06 part. The waxes and oil are melted together; the temperature is lowered to 170°F, and the sodium borate solution, also at 170°F, is added slowly while stirring thoroughly. When the temperature drops to 150°F, perfume is added, and the stirring continued until the cold cream is ready to pour at 130°F.

The mineral oil-base "cold creams" do not have the same penetrating and emollient effect as the official, expressed almond oil-base preparation. In reducing the proportion of beeswax in the cold cream ingredients below that prescribed by the USP, the resulting oil-in-water emulsion is more or less dependent upon the soap (sodium cerotate) formed by the reaction of sodium borate on the beeswax fatty acid. Boric acid is also a by-product of the reaction and acts as a preservative, making the addition of artificial preservative unnecessary.

Use of Hydrophilic Beeswax Derivatives. The modern use of hydrophilic derivatives of beeswax in the preparation of cold creams or the like makes it possible to incorporate more than the ordinary amount of water in the formulations, as exemplified by specific formulas. "Atlas 203" is as follows: mineral oil (65/75) 30; *beeswax* 12; "Atlas G-1704" beeswax derivative (*lipophilic*) 3.5; "Atlas G-1725" beeswax derivative (*hydrophilic*) 1.5; water 52; sodium borate 1 part; preservative and perfume, q.s. The waxes and oil are heated together at 70°C; the sodium borate and preservative are dissolved in water at 70°C, and the solution poured slowly into the wax-oil melted mixture with thorough agitation. The perfume is added when the cold cream has cooled to 50°C, and the cold cream is poured into the jars at 45 to 50°C, or it is tubed.

The use of sodium borate in cold creams has a tendency to eventually darken the surface when vanillin or like aromatic is used as a perfuming agent. It is possible to prepare a soapless, sodium borate-free, nonalkaline cold cream according to the following recipe: Mineral oil (65/75) 50; *beeswax* 7; "Tween 40" 2; "Atlas G-1726" *beeswax derivative* (hydrophilic) 8; and water 33 parts, preservative and perfume q.s. "Tween 40" is the trade name given to *polyoxyethylene sorbitan monopalmitate* by the Atlas Powder Company, Wilmington, Delaware.

Almond Cream. An almond cream, according to "Drug and Cosmetic Industry"[93], may be prepared from sweet almond oil 1 pound, *spermaceti* 2 pounds, *beeswax* 2 pounds, castile soap powdered 3 pounds, sodium borate

2 pounds, quince seed jelly 1 pound, alcohol 1 pint, water 4 pints. The spermaceti and wax are melted together. The soap and sodium borate are dissolved in hot water. These are mixed together and the balance of ingredients added. The mixtured is stirred and filtered before packaging. The texture of the cream can be improved by passing it through a colloid mill; this treatment improves the whiteness and makes the cream more fluffy. The use of spermaceti improves the gloss.

Vanishing Cream. A vanishing cream is a cleansing cream which has the tendency to absorb and leave no greasy film when applied to the skin. Partially saponified stearic acid or a stearic acid ester of a polyhydric alcohol is the foundation for such creams. The stearic acid derivative must be one which can be easily dispersed in water. Glycerol is an essential ingredient and keeps the cream from drying out. In some formulations white mineral oil (liquid petrolatum, light) is used as a softening agent. The wax ingredient may be *paraffine*, *spermaceti*, or simply *stearic acid* in excess of that required for saponification. Butyl-*p*-hydroxybenzoate is sometimes used as a preservative for vanishing cream. Some vanishing creams are opaque white, although a pearliness or silkiness is often desired and is brought about by the crystallization of the stearic acid, which takes many days to develop.

A vanishing cream may be prepared by melting *stearic acid*, 72 parts, in an enamelled double boiler, and adding to the melt slowly but with vigorous stirring a boiling solution of potassium carbonate 1, glycerin 25, and water 320 parts. *Triple-pressed stearic acid* is the preferred acid. After completing the emulsification, the temperature is lowered to 130°F, the perfume added, and the whole stirred from time to time until cold. It is well to allow the cream to stand overnight, stir the next day, and then pack into jars which are tightly covered immediately.

Glycerol serves as a humectant and is beneficial to the skin. Imported vanishing creams contain a high glycerol content, but American products usually contain only 5 to 10 per cent.

Examples of vanishing creams with a base of stearic acid ester of a polyhydric alcohol are: (a) white petrolatum 11, *paraffin wax* 133/135°F AMP 5, white mineral oil 20, *diglycol stearate* 16, glycerin 4, and water 70 parts, preservative and perfume a.q.s.; (b) white mineral oil 35, white petrolatum 5, *spermaceti* 15, *glyceryl monostearate* 12, glycerin 5, and water 45 parts.

Cleansing Creams. Cleansing creams are used for cleansing or removing the impacted greasy films from the skin. There are several commercial types of cleansing creams: (a) variants of regular cold creams, such as cleansing cold creams; (b) emulsifying types in which polyhydric alcohol fatty acid ester is used as an emulsifying agent; (c) lanolin-containing creams; (d)

liquefying types in which petrolatum, mineral oil, and waxes are blended but no water used. The term "facial cream" is applied to a cleansing cream the application of which is to be followed by some other facial treatment.

Cleansing creams are prepared in different consistencies, such as "soft translucent," "medium translucent," "medium opaque," and "hard opaque." In one of the emulsifying kinds, glycerin is used with water, *spermaceti* or *cetyl alcohol* is used as the wax, mineral oil as the emollient, and glyceryl monostearate as the emulsifying agent. In another kind, stearic acid is melted in mineral oil, *anhydrous lanolin* added, and the hot oil mixture poured into a warm solution of triethanolamine in water, vigorously stirring until a good emulsion forms. Carbitol and quince seed mucilate are then added. Perfume is mixed separately with propylene glycol and stirred into the cream after it has cooled somewhat. The whole emulsion is then stirred at low speed until thoroughly cool. In the liquefying type, *ceresin wax* is used with white petrolatum and mineral oil; *spermaceti* may be added to make the cream firmer if desired.

A cleansing cream containing magnesium hydroxide was patented by Walton[170]. It comprises *beeswax*, petrolatum, mineral oil, free magnesium hydroxide, and water. Walton also proposed a skin cream comprising petrolatum, *cholesterol*, *ceresin wax*, magnesium hydroxide, and water. A French letters patent granted to the Chas. H. Phillips Chemical Company[29] gives the following recipe for the skin cream: magnesium hydroxide 2.4, *cholesterol* 2.7, petrolatum oil 30.3, *ceresin wax* 1, water 60.4, ethylene glycol 3, and perfume 0.2 part.

Greaseless Cold Cream. There has been a market demand for a cold cream of a nongreasy type, one which will not leave an oily film on the skin, and which can be sold at a low price. These greaseless creams are somewhat similar to the type of vanishing cream which is formulated with a base of an ester of stearic acid with a polyhydric alcohol, but do not contain glycerin. The proportion of oil is also reduced appreciably below that used in the conventional cold cream.

Greaseless creams are prepared with *glyceryl stearate*, or analogous material, which will permit making the cream with a higher water content than that found in any of the regular types of cold creams. A greaseless cream is more readily removed from the skin by means of plain water than the regular cold cream, but it is not to be recommended for a very dry skin.

A cream of the greaseless type may be prepared from *white petrolatum* 6 *refined paraffin wax* 5, *glyceryl monostearate* 10, and white mineral oil 12 parts, with or without the addition of sodium borate to the water. The ingredients are melted together at 165°F and 50 parts of boiling water added while stirring with a forked blade. When the mixture becomes perfectly smooth and the temperature has been lowered to 130°F, a perfume such as

rose is added. The greaseless cold cream can then be poured into the jars at a temperature of about 120°F. Some recipes call for a refined *diglycol stearate* instead of glyceryl monostearate. If sodium borate is used it is added to the boiling water to the extent of 1 to 2 per cent. Preference is given to the nonalkaline creams which are considered nonirritating to sensitive skins.

Tissue Creams—Night Creams. The sale or distribution of emollient creams under the designations of nourishing cream, skin cream, tissue cream, rejuvenating cream, skin food, and the like has not been looked upon favorably by the Federal Trade Commission, since such names are considered misleading. *Night cream*, according to Kalish[96], is a descriptive term for fatty creams customarily applied for their emollient effect. These creams contain *beeswax, stearic acid, lanolin, cocoa butter*, arachis oil, cholesterol, water, sodium borate, and sodium benzoate. A few contain *spermaceti, cetyl alcohol*, soy lecithin, and *diglycolstearate*. The fatty layer of the skin is called "sebum," and contains saturated and unsaturated fatty acids, triglycerides, waxes, cholesterol (free and combined), and hydrocarbons including squalene. The night creams partially contain these constituents.

Tissue cream, one of the dermal cosmetics, fills a need for a cream that can be applied to the skin, especially the hands, to preserve it from prolonged contact with water, but which may be readily removed from the skin by soapy water. Generally speaking, such a dermal cosmetic is a modified cold cream, and is either of a nonalkaline or mildly alkaline type. Some of the tissue creams on the market (even though not designated as tissue cream) are water-in-oil beeswax-sodium borate emulsions" containing varying concentrations of lanolin.

A nonalkaline tissue cream (so-called night cream) may be prepared from *spermaceti* 10, *lanolin* 20, *glycostearin* 46, olive oil 20, almond oil 30, and water 50 parts, with perfume added. It is to be noted that the active ingredient is a vegetable and/or animal product easily absorbed by the skin upon which it has a softening effect. In this instance, olive and almond oils serve as emollients and *lanolin* as the most effective absorbing agent. Spermaceti serves as a hardening agent and as an emollient, and is a substitute for the wax of the dermal tissue. If a preservative is required, an ester of parahydroxybenzoic acid will prevent bacterial decomposition. Hydroquinone (0.1%) is useful as an oil-soluble antioxidant; recently *nordihydroguiaretic acid* has met with favor. A night cream of the kind described is a water-in-oil type, often preferred because of its oiliness. Another recipe for a similar type of tissue cream calls for: white mineral oil 18, *white beeswax* 2, *ozocerite wax* 2, *spermaceti* 2, *anhydrous lanolin* 2, water 8.5, and sodium borate 1.5 parts. The oil and wax ingredients are heated together in a double boiler, and 8½ parts of boiling water containing 1½ parts of

sodium borate are added with continued stirring in one direction. The temperature is lowered before the addition of perfume, and the cream poured into jars.

A recipe for an ordinary inexpensive night cream, but which is not a true tissue cream, is the following: *white petrolatum* 4, white mineral oil 10, *anhydrous lanolin* 6, *diglycol stearate* 15, water 65 parts, and a little perfume.

Hormone Cosmetic Preparations. The more expensive "hormone" cosmetic preparations are usually formulated from *beeswax*; cocoa butter; *cetyl alcohol*; cholesterol (0.5% or more); *p*-hydroxybenzoic ester as preservative; with or without sodium borate; perfume; and water. They occasionally contain *lanolin*, liquid paraffin, and a medium fatty cream base. Cholesterol has been indicated as suitable for inclusion in antisunburn preparations because of the tendency to produce vitamin D in the skin subjected to sunlight.

Absorption Creams. The ingredients employed in formulating what in the past was known as "nourishing creams" customarily included two or more of the following: *lanolin*, cocoa butter, coconut butter, *spermaceti*, *cetyl alcohol*, turtle oil, nut oil, and vegetable oil. The efficacy of such creams in actually nourishing the skin is questionable. The value of cholesterin, lecithin, vitamins, hormones, etc., is problematical; nevertheless there is a consumer demand for such creams. Typical formulations are: (a) *beeswax* 4, stearic acid 4, *lanolin* 10, cocoa butter 4, olive oil 40, cholesterin 2, lecithin 1, sodium borate 1, water 34 parts; (b) *beeswax* 4, stearic acid 2, *lanolin* 4, coconut oil 4, almond oil 50, cholesterin 2, lecithin 4, sodium borate 4, water 26 parts; (c) *beeswax* 10, *spermaceti* 3, cocoa butter 5, *lanolin* 6, olive oil 32, mineral oil 28, sodium borate 0.5, water 15.5 parts.

Vitamins A and/or F (*cis*-monoethenoid acid) are used as active dermal ingredients in some estrogenic absorption creams.

Specialty Creams. Fatty cosmetic creams which are characterized by the presence of some peculiar constituent such as turtle oil, avocado oil, or a medicament are referred to as *specialty creams*. "Turtle oil cream" has turtle oil as one of its emollients. Turtle oil is an oil which is thick at 15°C but fluid at 20°C, rich in cholesterol, and is slightly astringent; hence its value. The deodorized oil, mixed with an equivalent proportion of other nutritive oils such as almond or olive oil, is compounded with anhydrous lanolin and beeswax, and colored with an oil-soluble yellow. Turtle oil cream is prepared from: (a) *beeswax* 6.0, stearic acid 2.5, *lanolin* 5.0, cocoa butter 5.4, cholesterin 1.5, lecithin 3.1, turtle oil 26.4, almond oil 26.0, sodium borate 3.0, water 21.0 parts; or (b) *beeswax* 7.4, *lanolin* 13.0, turtle oil 25.0, almond oil 37.8, sodium borate 0.2, water 16.6 parts.

"Avocado night cream" is prepared from *beeswax* 10, *cetyl alcohol* 5, *lanolin* 7, grapeseed oil 42, avocado oil 10, sodium borate 1, and water 25 parts.

Another formula for avocado cream calls for a *lanolin absorption base, stearic acid, cetyl alcohol, beeswax*, almond oil, avocado oil, perfume, sodium borate, and distilled water. The sodium borate dissolved in hot water is added to the melted wax and oil ingredients, and the cream scented with perfume just before packaging. Cetyl alcohol acts as an emulsifier and stabilizing agent for an emulsion cream.

An emollient "day cream" for dry skin may be prepared from bleached *ozokerite* 4, mineral oil 16, *wool wax alcohols* 3, *lanolin anhydrous* 10, *stearyl alcohol* 3, and distilled water 64 parts. A preservative 0.2 per cent and perfume may be added.

"Cucumber cream" is similarly formulated, colored with a little green dye and perfumed with cucumber oil. "Lemon cream" is colored with tartrazine yellow and perfumed with the essential oil of lemon. "Almond cream" is perfumed with benzaldehyde. "Menthol cream" carries about 0.2 per cent of menthol. "Peroxide cream" is prepared by emulsifying *paraffin wax*, mineral oil, *lanolin*, a *fatty acid ester*, and hot water; the hydrogen peroxide and perfume are added when the temperature is lowered.

Cosmetic Cream Bases. In making specialty creams—creams which are highly colored, highly perfumed, or are to carry a medicament—it is desirable to start out with an emulsifiable base. Such a base may be prepared by adding concentrated potassium carbonate solution to melted stearic acid containing a little water, and then mixing the fused product with glycerol, anhydrous lanolin, and white beeswax after the evolution of carbon dioxide from the reaction of the carbonate and the acid has ceased. The base is made in the following approximate composition: *stearic acid* (free and combined) 35, potassium oxide (combined) 3, glycerol 51.5, *anhydrous lanolin* 7, and *white beeswax* 2.5 parts.

"Absorption base cream" is the name given to a cosmetic cream that is made from a base of lanolin, lanolin derivatives and concentrates, or cholesterol compounds. An absorption base cream is prepared much in the same manner as cold cream. It is a soft cream, nontacky and nongreasy to the touch, yet effective when used on dry skin. It is not unusual to combine with the lanolin or cholesterol compounds, such as *woolwax alcohols*, some white petrolatum and about 5 per cent of a fairly hard wax. The hard wax can be *ozocerite, beeswax, petroleum ceresin, "A-C Polyethylene,"* or the like. These absorption cream bases have varied uses in compounding cosmetics; for example, they are excellent in preparing sun-protective preparations and require only the addition of the sun-screening agent. Formulas for cosmetics sometimes refer to absorption cream base as "lanolin absorption base."

Foundation Cream. A so-called foundation cream for cosmetic use is formulated in such a manner that it will serve to lubricate the skin before

the application of face powder, and for the purpose of making the powder adhere to the skin. A foundation is customarily of the vanishing cream type, namely a composition which basically consists of stearic acid soaps and an excess of stearic acid (see section on Vanishing Cream, p. 671). A foundation cream of this kind may be prepared from *stearic acid*, *glyceryl monostearate*, mineral oil, potassium hydroxide, glycerol, water, perfume, and preservative. A foundation cream can also be made up of the absorption base type (see Cosmetic Cream Bases, p. 675).

The value of *microcrystalline waxes* in cosmetic dermatology has been advanced by Erich Meyer[116], particularly by the use of a microwax known in the trade as "Protowax." "Protowax" is produced in the same manner as petrolatum but is a cut made from slop-wax stock, and the finished sweated product has a melting point of 130°F. "Protowax" in appearance resembles a very stiff, white petroleum jelly. Since all of the occluded oil in the wax has been removed in refining it has the property of readsorbing oil. Its use in cosmetic creams is a means of preventing sweating. It is used in place of paraffin, or to replace part of the ozocerite. The type of microwax described is not only of value in cleansing creams, but in formulating solid brilliantines, perfume sticks, pomades, cream rouge, lipstick, etc.

Barrier and Protective Creams. Barrier creams are cosmetic protective ointments used by workers to protect their skin against injury from material with which they are working. For an oilproof barrier, a simple vanishing cream can be used; for a waterproof barrier a composition must be used which will fill the follicles of the skin with a harmless lipid material such as *lanolin*. Waterproof barriers are of value in protecting the skin against aqueous solutions of chemicals. The general requirements of a barrier are that it must be a nonirritant to the skin; it must be insoluble in the substance against which it gives protection; after application it should not make the dermal tissues either slippery or sticky; and it must be removed by ordinary cleansing methods. The most important need for the use of a barrier cream is as an industrial dermatitis preventative.

Barrier cream under the designation "protective cream" is used extensively by industrial workers to protect the arms and hands from grime, lacquer, solvents, etc. It can be readily washed off with water, by reason of a surface-active agent incorporated in the formula, such as "Tween 61" (Atlas Powder Co.). There are several kinds of such creams on the market. An example is one made by melting together *anhydrous lanolin*, "Tween 61," and castor oil; followed by *ceresin wax* and petrolatum; the product is poured into the containers just before it begins to set. Proportions of constituents are given in Atlas formula 55 as: "Tween 61" 5, *lanolin* 25, castor oil 25, *ceresin wax* (64°C/AMP) 5, and white petrolatum 40 parts. "Tween 61" is *polyoxyethylene sorbitan monopalmitate*, which is a tan-colored waxy

solid with a titer of 35 to 39°C, specific gravity of 1.04 to 1.08, flash point 460°F, and fire point 520°F.

Beeswax, cetyl alcohol, and *cocoa butter* are used in some formulations of barrier creams.

Barrier creams are said to reduce contamination of the hands by radioactive material, when used in conjunction with gloves made of rubber, isoprene, or PVC (polyvinyl chloride). The residual contamination with the use of the creams was easily removed by saturated potassium permanganate and sodium metabisulfite. [Tower, G. S., *Chem. & Ind.*, 1954, 387].

A "protective dressing," which may be mixed with medicaments, can be prepared by stirring a mixture of bentonite 7 parts and water 73 parts by weight, adding *petroleum jelly* (m. 110°F) with a consistency of 195 units (ASTM), and stirring until a smooth uniform paste is obtained for the ointment. (Patent of Chesebrough Manufacturing Co., Consolidated)[115a].

Special creams other than "protective creams" include *astringent creams, bleaching creams, acne creams,* and *estrogenic creams.* Astringent creams are emollient creams in which alum or some other astringent has been incorporated. Bleaching creams lighten the color of the skin; they contain hydrogen peroxide or other bleaching agent. Acne creams are intended to help minor lesions of the skin; they are emollient creams which contain benzoin or other active ingredient. Estrogenic creams contain estrogenic substances, improving condition and appearance of the dermal tissue. Hormone creams are estrogenic creams.

Creams protective against flash burns are on the other hand highly pigmented with titanium dioxide. Some protective creams of a water emulsion type are formulated using both "Span" and "Tween" emulsifiers, together with stearic acid, for example "Span 60," which is *sorbitan monostearate,* a waxy solid, and "Tween 60," which is an oily liquid. These nonionic emulsifiers find an extensive use in the preparation of drug and cosmetic emulsions.

Sun-preventative Cream. A typical composition of a cosmetic cream which will prevent sunburn is given by Newburger[124] as: *glyceryl monostearate* (self-emulsifying) 14.04; *anhydrous lanolin USP* 5.08; propylene glycol 5.08; titanium oxide 2.70; iron oxides 2.16; methyl-*p*-hydroxybenzoate 0.16; isobutyl-*p*-aminobenzoate 2.15; *isopropyl myristate-palmitate* 25.22; and water 43.41 parts, by weight. The investigator also prescribes certain methods of analysis for the quality of the ingredients in a cream of the kind described.

Hair Pomades and Dressings. Hair straightener is a pomade that is used largely for straightening negroid hair. It can be made according to the following formula: white petrolatum 6, *white beeswax* 1, raisin seed oil 2 parts by weight. The petrolatum is melted in a double boiler and the other

ingredients are then added. When the mixture begins to solidify a small amount of perfume is added. By increasing the amount of beeswax the product may be made stiff enough to cast into sticks if so desired.

Cream oil hair dressing is prepared from mineral oil, sorbitan sesquioleate, lanolin alcohols, *beeswax*, borax, and water. Sorbitan sesquioleate is a water-in-oil emulsifying ester which is also of considerable value in the formulation of foundation creams. *Cetyl alcohol* is used in some hair cream formulations, as is also *ceresin wax*.

Facial Make-Up. A facial make-up is a cream which is formulated from pigment, colors, a hard wax capable of producing a luster, and low melting point esters. The pigment may be a mixture of titanium oxide and talc. A preferred wax is *carnauba wax*, which comprises 5 to 10 per cent of the make-up. The most satisfactory esters are those prepared by esterifying a fatty acid in the C_{12} to C_{18} range, with a low molecular weight alcohol, as for example, isopropyl alcohol. An ester such as *isopropyl myristate* can be used in the formulation. A myristic acid containing small amounts of lower and higher homologs as impurities is satisfactory for the preparation of the ester. Mineral oil may be added to the cream to increase the oiliness or sheen of the film produced by the cake. Facial make-up is also marketed in stick form.

Depilatory Wax. A depilatory (or depilating) wax is a wax which in the melted condition is applied to the surface to be dehaired, in a manner that there is no injury to the skin. Generally a resin is incorporated in a mixture of waxes; for example, a depilating wax may be prepared from water-white rosin 50, *yellow beeswax* 27, *paraffin wax* (130/132°F) ASTM 18, petrolatum 5 parts, with perfume added. In its preparation the rosin and waxes are melted together and mixed, the petrolatum is added, and then when the temperature drops to 60°C the perfume may be added, and the product poured into suitable molds.

Nail Polish Remover. Nail polish removers may be prepared from emulsifying wax (e.g., "Lanette Wax SX"), "Tween 60," castor oil, butyl acetate, and water, all properly proportioned.

Waterless Hand Cleaners. Hand cleaners of the waterless type are products designed to removed various types of dirt from the hands without requiring washing or rinsing with water. These are provided as pastes, then creams or liquids. Although many of the commercial waterless hand cleaners have soap as a base, there are several which have wax as the basic ingredient, and these are closely related to cosmetic cleaning creams. In their preparation the emulsifying agent may comprise glyceryl monostearate, alkali, and water, used to emulsify a melted mixture of *stearic acid*, mineral oil, *paraffin wax*, and *spermaceti*. *Lanolin* is also used in some of the waterless hand cleaner formulations, with or without the addition of "*Carbowax Compound* 4000."

Cream Rouge. The word "rouge" literally means red, although it properly includes all products intended to impart a glow to cheeks and lips. The term, however, has gradually become limited to colorings applied to the cheeks. Rouge for the lips is now very largely made in sticks and is called lipstick. Rouge is available in several forms: (1) creams, (2) pastes, (3) compact powder, and (4) liquid. Rouge in the powdered form contains no wax. The term "rouge" is also given to colored powder, usually red oxide of iron, used in polishing powder for glass, metal, gems, etc. When the rouge is made up into a pasty consistency for cosmetic use it is called "cream rouge." Cream rouge is recommended for skin that tends toward dryness, and light weight powder should be applied over it. The pigment is dispersed in an emulsion that conforms to the type of cream employed, whether cold cream, emollient, or vanishing cream. Some preference is given to the vanishing type. The pigment is usually an organic lake, and the dye one of the fluorescin group, similar to those colors employed in the manufacture of lipstick. The white base foundation always contains one or more waxes—*beeswax*, *spermaceti*, *cetyl alcohol*, etc.—the nonhydrocarbon waxes being preferred over hydrocarbon waxes like paraffin. For example a cream rouge of the paste type may be prepared from *beeswax* 2, *cetyl alcohol* 2, cocoa butter 3, *spermaceti* 3, liquid paraffin 10, white petrolatum 30, and color. The color-lake and dye- is added to the waxes melted in the oil, and the whole mass is mixed and milled.

Lipstick. Lipstick is a rouge for the lips in the form of a stick or pencil. It is made up of five elements: wax, dye, pigment, emollient, and perfume. The emollient used for the purpose should not only act as the softening agent but provide a mutual solvent for the other ingredients. The dye acts as a hue toner to the pigment. Care is taken in the selection and use of dye fixatives so as to obtain uniformity of color and shade. In the earliest lipsticks the wax was chiefly *lanolin*. The demand for a firm lipstick pencil has led to compositions of harder waxes with or without lanolin. A selection is made of one or more of the following waxes: *beeswax*, *ceresin*, *ozocerite*, *carnauba*, *candelilla*, *spermaceti*, *cetyl alcohol*, *stearyl alcohol*, *hydrogenated vegetable oil*, *diglycol stearate*, *petrolatum*, and *white microcrystalline petroleum wax*.

The dye used to the greatest extent in lipstick manufacture is commonly referred to as "bromo-acid." Bromo-acid refers to mono-, di-, or tetra-acid salts of fluorescein. For example, eosin, which is the potassium salt of tetrabromofluorescein, is commonly used. The dibromofluorescein imparts a different hue in the nature of an orange yellowish stain. Phloxin, the potassium salt of dichloro- or tetrachlorobromofluorescein, and erythrosin, the sodium salt of diiodotetrabromofluorescein, are also used as dyes. The pigments are coal-tar lakes or natural oxides, but usually lakes such as geranium red, rhodamine tolu-safranine, lithol red, ponceaux, etc. A color

fixative commonly used is castor oil. So-called solutions of bromo acids, e.g., "Bromosolves" (Givaudan-Delawanna, Inc.), are offered on the market to blend with the lipstick wax foundation. Tetrahydrofurfuryl acetate is a solvent, particularly for eosin which it dissolves to the extent of 28 per cent.

German dye solutions for coloring lips consist of (a) "Eosin acid L, new" 5 g, and rosin (or other suitable resin) 15 g, in a solution of ethylene glycol monomethyl (or monoethyl) ether 50 cc and ethyl ether 50 cc; or (b) "Rhodamine base B extra" 7.5 g, rosin (or like) 10 to 15 g in solution of 100 cc of solvent described; or (c) a 1:1 mixture of (a) and (b).

Since the enactment of the Federal Food, Drug and Cosmetic Act of 1938, all colors for use in cosmetics have been under strict regulation. The colors used must be certified by the Food and Drug Administration.

The emollients include almond oil which was in very early use, lanolin absorption base, white petrolatum, liquid paraffin, cocoa butter, and benzoinated lard. Stearo-resorcinol, or a mixture of polyhydric alcohols, and glyceryl monoricinoleate are extensively used.

Ordinary lipstick contains 2 per cent of bromo acid, and 3 to 10 per cent of colored lake, in sufficient base to finish 100 per cent lipstick. The white base might consist principally of *beeswax* and castor oil, modified by a little *white petrolatum* to soften it and make it spread more rapidly on the lips. Castor oil dissolves only 0.2 to 0.3 per cent of the bromo acid, tetrabromo- and dibromo-fluorescein; castor oil is nevertheless a good carrier of bromo acid. Furfuryl alcohol and its acetate, diethyl sebacate, and dibenzyl sebacate, are all good solvents. Diethyl sebacate is superior for lipstick purposes to the dibenzyl ester, except at consistently elevated temperatures. Navarre[121] states that butyl stearate is a better bromo acid solvent than is castor oil, and that it is sometimes used to cut the thickness of castor oil films; its disadvantage is its tendency to bleed out.

Isopropyl myristate is a good dispersing agent like castor oil. White oleyl alcohol has also proved serviceable.

The dye and its fixative (bromo acid solution) may constitute nearly one-half of the lipstick composition, the remaining half is a white foundation which consists of *beeswax*, *carnauba wax*, *ozocerite*, *spermaceti*, *lanolin*, *petrolatum*, etc. Perfume is used to the extent of less than one per cent in the milling of the colored composition just prior to casting.

Polyhydric alcohols or their derivatives, waxes, hydrogenated oils, triethanolamine, and stearic or white oleic acids, have been reported as ingredients of French lipstick.

Beeswax is used in lipstick for its binding property; in addition it gives body and drag, and raises the melting point. Its use aids in expelling the finished stick from the mold in making lipstick. *White beeswax* is used in

the proportion range of 5 to 40 per cent, customarily about 15 per cent; too much of the wax will produce an undesirable granular lipstick. *Carnauba* and *candelilla waxes* give luster and hardness, but must be used sparingly such as 3 per cent; otherwise they make the lipstick brittle. *Lanolin* and *lanolin absorption base* possess emollient properties, and by acting as binding agent for other constituents tend to minimize sweating and cracking of the stick and give it a certain degree of plasticity. White mineral oil gives the much desired gloss, and makes the stick spread more smoothly and with less tackiness. It has no solvent power for the bromo acid.

Petrolatum has been used to the extent of 20 to 25 per cent, but Navarre[121] noted that it causes the stick to drag too much. It can be satisfactorily used to the extent of about 10 per cent. *Bleached ozocerite* aids in securing a fine-grained white foundation of suitably high melting point and assists in retaining the oils in the wax structure.

In lipstick manufacture it is well to use waxes of high melting point. The lipsticks on the market have a variable melting point ranging from 55 to 60°C (131 to 140°F). *Cetyl alcohol*, according to Harry[81], has an unctuous effect and should not be used to exceed 4 to 5 per cent. It is a good solvent for eosin or like color and helps in the permanence of the stain. Preference is also given to cetyl alcohol because of its nice feel to the lips, but the use of both cetyl alcohol and *spermaceti* is limited because of their friability. When used together in the white base they should not constitute much more than 5 per cent of the finished lipstick. Pure *stearyl alcohol* melts at 52°C and has been used as a higher melting replacement for cetyl alcohol. It is a solvent for bromo acid. *Cocoa butter* combines hardness with low melting point and excellent emollient properties, although it tends to bloom unless partially hydrogenated. Cocoa butter has a smooth effect on lipstick but should only be used as a minor constituent. The so-called *white absorption bases* contain lanolin, refined lard, hydrogenated oils, etc. The lipstick material without the added color is known as the "white foundation."

A typical formula for white foundation would be lanolin absorption base 16, beeswax 15, ceresin 3, white microcrystalline wax 8, cocoa butter 10, and liquid paraffin 5 parts. Another example would be cocoa butter 6, stearic acid 3, cetyl alcohol 2, liquid paraffin 5, spermaceti 6, beeswax 20, lanolin 8, benzoated lard 20, and castor oil 5 parts. A white foundation for suitable use with "Bromosolves" has been given as carnauba wax 3, beeswax 15, ozocerite 5, spermaceti 4, cetyl alcohol 1, lanolin 11, and petrolatum 10 parts.

Wetting agents as well as perfumes find a use in lipstick manufacture. Perfumes in lipstick are coumarin, methyl coumarin, ethyl vanillin, and vanillin in conjunction with orange blossom, rose, and jasmine bouquets.

The principle in the formulation of the mass for lipstick can be illustrated

by a study of the white base foundation. For example, should we combine beeswax with castor oil we would secure good casts, but lack of luster, and the stick would leave a thick film. If we incorporated sesame oil and anhydrous lanolin in the mass, we would get a stick that would give a thinner and better adhering film, and so on. In formulating lipstick it is necessary that the texture be soft and creamy; suited for use in both hot and cold weather, that is, it must neither drip nor crack; and further it must be in a condition to apply to the lips with a minimum amount of pressure. In lipsticks made with bromo acid as the sole coloring, the orange tint is changed on the lips to red.

Black lipstick is prepared with a so-called "magic black," of which one per cent is added to the lipstick base. Although the lipstick pencil looks black, it rubs out to a deep red hue on application to the lip. "Personality lipstick," popular at one time, had a dye sensitive to slight changes in the pH value of the saliva.

Lip-rouge has also been prepared in liquid form, as in the composition invented by Grate[73e], namely isopropanol 70, soybean lecithin 5, *hexadecyl* (cetyl) *alcohol* 1, tincture of benzoin 5, dye 0.5, and perfume 0.4 parts by weight. The dye was dissolved in the isopropanol, and heated to just below the boiling point. After cooling the remaining ingredients were added in the following order: soybean lecithin, tincture of benzoin, hexadecyl alcohol, and perfume. Grate claims the following properties for the liquid lip-rouge: moistureproof, softening, healing, is thinly applied, rubs off under relatively high pressure, relatively long lasting, nonflaking, nonpeeling, provides velvety appearance, remains in solution, nonrunning, and can give two shades from the same color by application of two thin layers.

Manufacture of Lipstick. There are several stages in the manufacture of lipstick which involve operations of melting, milling, casting, removing, flowing, and filling the lipstick in holders. The customary procedure is to melt the fats and waxes and then keep the melt at a minimum temperature so that the pigment can be milled in. The dyestuff, bromo acid, is dissolved in the liquid ingredient, or emollient, after which this dye solution is added to the pigmented base, and the whole subjected to remilling. These milling operations are conducted and regulated by means of heat control. Triple-roll mills are superior to two-roll mills since they almost double the output. Small producers generally use a 6-inch three-roll mill. For larger outputs a 16-inch three-roll mill is employed. The process takes a little longer than with some homogenizers, but the extra time spent is amply justified by the improved results.

In milling pigments it is perhaps best to use part of the fluid content, with part of the petrolatum and lanolin, to make a paste, and this should be stiff enough to be removable from the receiving plate with a wide spat-

ula, or wallpaper scraper. It is then added to the hot mass, stirring slowly with each addition. When the mass is freed from air and sufficiently cooled it is run into the sectional mold which has a series of cavities, all made of brass. The pattern consists of two halves which are capable of being clamped together for filling and taken apart after the sticks have been formed. The sectional mold is refrigerated and the sticks are removed when cool. A smooth finish is imparted to the sticks by passing them through a small flame, a practice which is not universal. After this they are cased in a metal or other suitable holder.

Ball-point Lipstick. A lip-rouge in a ball-point, pen-type dispenser, under the name of "Bolero" (Frank Charmel, Inc., New York), is said to be a cream with a lanolin base which rolls onto the lips, giving the same intensity of color with a lighter application than conventional lipstick. The dispenser is a cylinder about four inches long made of a rustproof metal. It is fitted with a small steel ball at one end, and the tube has a screw-cap at the other end which can be turned to increase or diminish the flow of the lip cream. A metal cap fits snugly over the ball point. Refills are available wrapped in hermetically sealed acetate tubes.

Lipettes. "Lipettes" is the trade name given to lipstick which is made up in the same form as "book matches." The die that cuts the "stems" and forms the comb performs its function so that each stem is completely separated as to permit individual heads to be formed in the subsequent dip bath of bromo-acid rouge composition.

Eye Cosmetics. The principal cosmetics for use about the eyes are *eyebrow* pencils, mascaro (Spanish for mask, also *mascara*), and *eye shadow*. All three preparations require wax in the foundation. Eyebrow pencils were formerly made in the form of wax crayons in metal holders, but these have been supplanted by wooden pencils in which the pigmented wax forms a soft core, which can be handled and sharpened just like writing pencils. They are available in black, dark brown tones, and lighter golden browns. They may be prepared from beeswax, hydrogenated cottonseed oil ("Coto" flakes), cocoa butter, carton oil, and lanolin absorption base. The black color is lampblack, the brown, one of the umbers, burnt siennas, etc.

Mascaro is made in the form of (a) cake, (b) cream, or (c) liquid. The cake is the most popular and successful form for a temporary coloring applied like a paint to the eyelashes. The colors are customarily black, blue, or green. When mascaro is to impart luster as well as color to eyelashes, it is made as a greasy type, e.g., a mixture of beeswax, spermaceti, stearyl alcohol, cocoa butter, and petroleum jelly, combined with Oil Blue B. Cakes of mascaro are made by melting all the ingredients, passing them through a mill for thorough mixing, and finally through a warmed plodder. The plate of the plodder will have been so perforated that it will extrude a

strip of the desired thickness. This strip is cut or stamped into cakes of the correct size and boxed. For example, the package may contain a small bar (6 × 1 × ½ cm) with brush which may be wetted for its application. A mascaro suited for molding may be formulated from white oleic acid, methanolamine, stearic acid, carnauba wax (⅓ of composition), petroleum jelly, lanolin, perfume, and color.

A mascaro of the cream type called "Creme mascara" may be made from a melt of beeswax, glyceryl monostearate, petroleum jelly, and stearic acid; color (e.g., carbon black, or burnt sienna) is added to the hot melt and then the mixture milled with a small amount of hot aqueous solution of gelatin and triethanolamine. Another formulation calls for beeswax, cottonseed oil, turpentine, distilled or deionized water, triethanolamine, color, and perfume. The beeswax constitutes 25 to 30 per cent of the whole. The mass is allowed to stand several days before filling. "Creme mascara" is packaged in small metal tubes, labeled with color, accompanied with a small brush for its use on the eyelashes.

Liquid Cream Shampoos. Liquid cream shampoos are either of the soep or soapless type. *Sulfated* and *phosphated alcohols* of the higher fatty acids (C_{14}, C_{16}, C_{18}) are very important wetting agents and detergents, and likewise are very effective in the production and maintenance of emulsions of the oil-in-water type. They are useful in the manufacture of soapless shampoo. The alcohols used for the purpose are *cetyl* and *stearyl*, and according to Redgrove[188], are effective in concentrations as low as 1 to 2 per cent of the sulfated alcohol mixture. Soapless shampoos can be made of the lathering and nonlathering types. Shampoos should be neutral or slightly acid.

Wax alcohols partially sulfated or phosphated are compounded with an emulsifying agent, water, and a small amount of wax such as *lanolin*, *paraffin*, or *beeswax* to produce a liquid shampoo. An example of a liquid shampoo is the following: fatty alcohol sulfate A 30, magnesium stearate 1, polyvinyl alcohol (100 per cent solution) 20, methyl cellulose (3 per cent solution) 9.5, water 38, lanolin 0.5, and glyceryl monolaurate 1 part. Fatty alcohol sulfate A, also known as "Duponol WA Paste," is a white paste at temperatures below 27°C. A shampoo of the pearly paste type can be formulated from: fatty alcohol sulfate A 40, sodium stearate 8, water 41, and lanolin 1 part. (Also see Section on Wax Alcohols as Cosmetic Ingredients, p. 686).

Shampoos may also be made by the treatment of sulfurized fatty acids with partial saponification by means of triethanolamine (TEA). Castor oil which has been heated with sulfur and iodine as a catalyst, washed with water, dried, and refluxed with ethanol, or a *sulf-olive oil* similarly produced, may be partially saponified with TEA, and made into shampoo in which

lanolin or a suitable wax is incorporated. According to Dearborn[43] the sulf-oils, *sulf-castor oil*, and the like are of general value in cosmetics. A concentration of 10 to 25 per cent of the sulf-oil in ethanol produces a hair preparation, so-called hair tonic. Cosmetic creams may be prepared from mixtures of ethyl 9,10-thiooctadecanate, *lanolin*, *beeswax*, *paraffin wax*, glycerol, and water; and heavier creams by replacing the octadeconate with sulf-olive oil.

So-called transparent "sudsing" shampoos can be prepared by the addition of polyol ethylene-oxide ether-ester derivative of alcoholized lanolin, to soap solutions. *Polyoxyethylene sorbitol lanolin derivatives* (G 1425, 1441, 1447—Atlas Powder Co.) are of that nature. The derivatives are also useful in preparing oil-in-water cosmetic emulsions from a cosmetic cream base of stearic acid, beeswax, and mineral oil. *Polyoxyethylene sorbitol beeswax derivatives* are also incorporated in creams which are to be made into liquid cosmetic preparations.

Brushless Shaving Cream. Latherless or brushless shaving creams are to some extent replacing the lathering type of cream on the market. A brushless cream, like an oil-in-water vanishing cream, is generally prepared from partially saponified stearic acid, or stearic acid and a relatively small amount of a saponifying agent; an emulsifying agent; an emollient; water; and a wax to give proper consistency to the emollient, which is either a mineral or a vegetable oil. Very small amounts of perfume, and occasionally preservative and pigment, are incorporated in the cream.

The wax constituent is one selected from one or more of the following: *anhydrous lanolin*, *spermaceti*, *cetyl alcohol*, *beeswax*, *Carbowax*, *polyhydric alcohol ester*. A shave preparation in stick form by Thomas and Whitham[162] (patent assigned to Lever Brothers) is composed of sesame oil 38.75, *spermaceti* 45.0, stearic acid 7.5, tallow soap 1.5, partial polyglycerol fatty acid esters 4.0, titanium oxide 2.0, and perfume 1.25 parts, and a requisite amount of water. Glyceryl or a glycol stearate may be used as the emulsifying agent.

A formulation of brushless shaving cream, which employs anhydrous lanolin as the basic wax constituent, is given as follows: stearic acid, triple pressed 35.0; mineral oil, white 7.5; lanolin, anhydrous 6.5; terpineol 0.1; triethanolamine 2.2; sodium borate 2.2; propylene glycol 4.0; and water 145.0[9b]. Other formulations are: (a) water 70.0, stearic acid 16.5, lanolin (anhydrous) 3.9, mineral oil (white) 3.5, triethanolamine (TEA) 1.0, sodium borate 1.0, carbitol 1.5, propylene glycol 2.55, and preservative 0.05 parts; (b) stearic acid 18, lanolin (anhydrous) 3, white mineral oil 3, glycerol 5, TEA 2, sodium borate 2, water a.q.s. to make 100 parts, perfume trace.

The customary procedure for the making of brushless creams is as fol-

lows. The stearic acid is melted with the wax (e.g., lanolin, anhydrous) and mineral oil, and brought to 70°C. The water containing the TEA and sodium borate is separately heated to the same temperature. The wax-oil is then added to the aqueous solution with vigorous stirring. The whole is mechanically paddle-stirred (to avoid combing) whence a smooth emulsion is obtained. When cooled to about 50°C the emollient (e.g., propylene glycol) in which the perfume has been dissolved is added. The cooled cream is allowed to stand overnight and stirred again for about one minute before packaging.

Matumoto[114] reported that an analysis of Mollé shaving cream revealed that it consisted of: water, 70.80 per cent; Na_2O, 0.394 per cent; combined stearic acid, 3.31 per cent; free stearic acid, 14.20 per cent; *spermaceti*, 3.75 per cent; and liquid paraffin, 7.55 per cent.

A material of protein origin may be used as an emulsifying agent in the preparation of brushless shaving cream, e.g., mazein (zein), soy casein, quince seed, sodium alginate, etc. An emollient is added to soften and keep the cream from drying out in storage. An example of a cream with a protein material constituent is given in the following recipe: stearic acid 20, *cetyl alcohol* 1, *lanolin anhydrous* 0.5, *beeswax* 1, sodium hydroxide 1.4, water 70, soy casein fine 5, and preservative 0.2 parts.

Face Powder. Face powders of superior quality are made with naturally bleached granules of *white beeswax*, or *vacuum distilled beeswax*, as an important ingredient. A formulation for such a powder is: specially prepared beeswax white 5, starch 10, very finely powdered light kaolin 5, talc 5 parts, coloring and perfume to suit. The mixture is finely powdered and sifted. In cheaper powders stearates are used instead of beeswax.

Wax Alcohols as Cosmetic Ingredients. *Myristyl*, *cetyl* and *stearyl alcohols*, because of their wax-like properties, have found important places in wax technology. *Lanette wax*, made in England, consists of a mixture of myristyl, cetyl, and stearyl alcohols which has more or less been sulfated, or phosphated, and is used extensively in formulating skin creams, ointments, etc. More recently *cetyl alcohol* has loomed in importance as an ingredient in ointment bases, superfatted cosmetics, lipstick, cream rouge, beard softener, nail softener, shaving soaps and powders, and massage-, vanishing-, or tissue creams.

Cetyl alcohol in its pure form is prepared by the saponification of spermaceti by potassium hydroxide, and then separation of the alcohol from the unsaponifiable matter. Cetyl alcohol is insoluble in water, but soluble in alcohol, chloroform, ether, the glycols, and aromatic hydrocarbons. It mixes with fats and oils, and is tasteless, odorless, and nonirritating. On application to the skin it renders the surface velvety, rather than smooth and slippery. It is not affected by acid, alkali, light, or air, and does not

become rancid. Cetyl alcohol has been found helpful in creams for the treatment of eczema and pruritus. A commercial powder for such cases has been prepared from equal parts of boric acid and cetyl alcohol. According to Goodman and Suess[72], cetyl alcohol forms water-absorbent emulsions, facilitates the inclusion of various medicaments, is readily incorporated in compounded ointments, and is claimed to aid in the passage of certain medicaments through the epidermis. Cetyl alcohol may be regarded as of general value is cosmetic dermatology.

Thiele's[160] cetyl alcohol ointment is prepared from *cetyl alcohol* 5, *anhydrous lanolin* 5, *paraffin wax* 15, white petrolatum 50, and liquid petrolatum 30 parts. The waxes and petrolatum are made into an ointment with water in the customary manner of preparing a cold cream. The finished preparation is a beautiful, white, creamy substance which, when applied to the skin, does not look oily and is said to be completely absorbed.

The U. S. Pharmacopoeia recognizes an ointment which is estrogenic and beneficial to the skin. It is known as *hydrophilic petrolatum*, and is formulated from *cholesterol* 1, *stearyl alcohol* 3, *white wax* 8, *wool wax* 15, and *white petrolatum* 73 parts. In its preparation the stearyl alcohol, the waxes, and the white petrolatum are melted together on a water bath; then the cholesterol is added until it completely dissolves. The mixture is then removed from the water bath, and stirred until it congeals.

Hydrophilic Properties of Ointment Bases. The hydrophilic properties of ointment bases may be determined by "water number," as defined by Casparis and Meyer[27]. *Water number* is the maximum quantity of water capable of being held at ordinary temperature (about 20°C) by 100 grams of a water-free ointment basis. For example, petrolatum has a water number of 8.1 to 15.6, *woolwax* 185.6, petrolatum plus *spermaceti* 11.1 to 13.6, petrolatum plus *woolwax* 78.5 to 88.6, petrolatum plus *cetyl alcohol* 38 to 51.5, hardened peanut oil 75.4, etc.

Halpern and Zopf[77] also advanced a method, in which water is added, 0.5 ml at a time, to 10 grams of a petroleum-wax mixture; the wetted mixture is triturated in a mortar until no exudation is noted on spreading of the mixture. They studied the hydrophilic properties of five saturated fatty alcohols, C_{10}, C_{12}, C_{14}, C_{16}, and C_{18}. *Cetyl alcohol*, C_{16}, has the lowest optimum concentration, and *stearyl alcohol*, C_{18}, the highest *water number*. The C_{10} and C_{12} alcohols yielded an objectionable odor. All the resulting emulsions are of the water-in-oil type. The effect of the addition of one or two alcohols and *woolwax* to petrolatum was studied at the optimum concentration of the alcohols. In the first case the water number of the mixture was lower than the sum of the individual water numbers, and in the latter it was roughly equal.

Stearyl alcohol (m. 56–60°C) is used with lauryl sulfate to produce stable

oil-in-water creams, and yields a somewhat firmer preparation than cetyl alcohol. Anhydrous mixtures for making hydrophilic ointments may be compounded from (a) *stearyl alcohol* 53, *cetyl alcohol* 7, polyethylene glycol "400" 38.6, sodium lauryl sulfate 1.5 parts; or (b) *stearyl alcohol* 64.7, *cetyl alcohol* 8.6, "Carbowax 1000" monostearate 13.0, "Carbowax 1540" 8.7, and anhydrous lanolin 5.0 parts.

WAX IN CRAYONS AND LEAD PENCILS

The word "crayon" as originally defined covered a drawing material, generally in the form of a pencil, but sometimes in powdered form, employed by the artist for drawings. The crayons were made in black, white, and red colors; the black and red were used for outline and shading, the white to heighten lights. Although originally prepared from vine black, native earth, and other compact, friable mineral substances, crayons are now for the most part artificially prepared mixtures of a base of prepared chalk, and pipe or china clay with Prussian blue, chrome yellow, vermilion, ochers umbers, and other pigments cemented together by the introduction of some weak adhesive, usually gum tragacanth. Calcium gypsum, steatite, and compounds of magnesium, bismuth, and lead are occasionally used as a base. In one form of hard crayon, talc, barium sulfate, kaolin, calcium sulfate, pigment, and adhesive are mixed and molded with water, dried, and then immersed in melted wax. A formula for making waxless crayons, which is given by Smith[164], consists of a mixture of clay 75 lb, chalk 75 lb, starch 30 oz, alcohol 2 oz, soap 12 oz and water 4 gal. Hard wax crayons are made today in many striking colors with a base of stearic acid and about half as much paraffin.

Wax Crayons. The manufacture of crayons consists of preparing and then molding a mass of waxy material in which color has been incorporated. One method (a) consists of mixing the powdered color and steatite, or its equivalent, together with a suitable amount of the stearic acid base in a closed rotating cylinder or ball mill, and continuing the rotation until the mixture is uniform in color; or (b) the wax and/or fat acid may be sprayed on a powdered crayon compound, such as pigment and magnesite, and mixed well. In the latter method (b) the mixture is placed in a mold, and heated in order to allow the wax and fat acid to penetrate uniformly into the compound. The method is suited to preparing paper-encased thick crayons.

The amount of color used is proportional to the wax and varies according to hue, and its color strength. Between 8 and 25 pounds of color are used to each 100 pounds of base wax. Tints are made by using the pigment lithopone with the color; for white crayons the lithopone is used alone. In the first method (a) the mixture from the ball mill is made into a paste with a

thin size, and kneaded to secure uniformity. The paste is then compressed in a horizontal brass, bronze, or stainless steel cylinder having at one end a plate with an orifice slightly larger than the diameter to which the crayons are to be made. The paste is of such a consistency that a slight pressure will force it out of the orifice in front of the cylinder at a regular rate. The piston is put in position and the mass forced by uniform gentle pressure out of the narrow opening. The conveyor belt must move away at the same rate as the rod is ejected from the cylinder, so that a long stick of crayon mass rests upon it. This stick is cut up by a blunt knife into uniform lengths, which are dried upon boards with an absorbent paper. The rods shrink somewhat on drying, and when dry they are enclosed in casings similar to those of the ordinary lead pencil.

There is another process (c) in which a thick paste is molded into blocks of the length of the crayons. These blocks are slowly dried at a uniform temperature and sawed by a fine saw into thin rods which are enclosed in a wooden case. The powder from the sawing is used in the next batch. The disadvantage of this method is that it is difficult to avoid cracks in drying the blocks, and a large number of the sawed blocks break, even with the most careful treatment.

One Japanese patent [Chigusa, L., Jap. 1078 (1950)] claims a composition for crayons of japanwax 20, hydrogenated oil 15, and camphor 30 parts, which mixture is heated to 180°C. Then 10 parts of paraffin wax are added and the mixture cooled to 100°C, when 15 parts of calcium carbonate and 15 parts of pigment are added. The substance is molded while hot and then cooled. In another Japanese patent [Matsui, K., Jap. 1077 (1950)] one part of a 3 per cent solution of ammonium ricinoleate is dissolved in 100 parts of benzene, and 50 parts of glycerol added. The mixture is emulsified and added to 20 parts of melted soft paraffin wax, mixed with 100 parts each of pigment and magnesite at 40°C, molded, and dried.

The colors used in crayon manufacture include lampblack, dip black, chrome yellow, primrose yellow, Indian red, Tuscan red, Prussian blue, raw umber, burnt umber, raw sienna, burnt sienna, American vermilion, French ochre, rose pink, Vandyke brown, rose lake, Venetian red, and chrome green (light, medium, and dark). Colors are composited to produce other hues; for example, purple lake, para red, and lithopone are combined to give a purple of desired tone.

Pastels. Pastels are crayons that are made of coloring material diluted with a white base. They are made up into cylinders or pencils with the least amount of gum necessary to hold the particles of color together in the lightest possible manner, so that a touch of the pencil on the surface of the paper leaves an impression. Pastels for use by artists are sold in a series of tones, usually six in number, the darkest pencil consisting of pure color; all

the other pencils of the series are mixed with white to a greater degree as they ascend the scale towards the lightest. Thus the artist can select a certain number of tones ready to use at once. A pastel can be applied as a pencil by means of lines or short strokes, or it may be rubbed using the tip of the finger as a pad.

What is commonly known as a wax drawing pastel is somewhat different from the original artist's pastel crayon. The composition may consist of hard soap, wax, and color. *Beeswax* and *spermaceti* are suitable wax materials. The melted waxes and the hard soap are mixed with the pigment and the mass ground until smooth in a heated mill. The finely ground pasty mass is then poured into water so as to secure binding of the colored wax material. In a white ground mass, white lead, zinc white, pearly white, or titanium oxide may be used to intensify the whiteness. Although gum tragacanth is a common agglutinant, glue and gum Senegal, or acacia, are also used. Oils, fats, and wax serve as emollients and produce gloss when so desired.

Ethyl cellulose and cellulose laurate have been proposed as wax adjuncts which will strengthen the crayon in the longitudinal direction by providing small stringy particles. These cellulose derivatives can be dissolved at an elevated temperature in *stearic acid*, or in a mixture of waxes—*ceresin*, *carnauba*, *beeswax*, *paraffin*, etc. Polyethylene wax when added to the extent of 2 or 3 per cent to paraffin will strengthen the crayon. The Eagle Pencil Company, in 1936, obtained a Canadian letters patent[51] for a pencil or crayon in which a filler and a pigment are united by a binder that includes water-soluble etherized cellulose and also small stringy particles of water-insoluble cellulose, and a waxy substance composed of a mixture of stearic acid and a wax.

Marking Crayons. A crayon that is used exclusively for marking is made in a different manner from the artist's crayon and usually of much cheaper material. The manufacture of cheap wax crayons with paper wraps is not unlike that of candles, both in procedure and material. Marking crayons are made of different compositions in accordance with the material to which they are applied, e.g., leather, cloth, metal, glass, cardboard, etc.

A French crayon made by Sciffini for ground marking is prepared from colophony 20, stearin 15, *yellow wax* (beeswax) 10, and chrome yellow 20 parts. A crayon for marking textile fabrics, as made by Beckers[12], is formed of *stearic acid*, barium sulfate, and starch. A tailor's marking crayon requires a hard wax like *carnauba* blended with *paraffin wax*, and pure white talc. A glass marking crayon must be fairly soft and is made from paraffin, a little stearic acid, and para red or other color. Weil[173] has proposed a

luminous writing-stick composition made of *japanwax*, *ozocerite*, *paraffin*, and petroleum jelly, together with a small proportion of luminescent sulfide.

Graphite Pencils. Graphite leads for pencils are made by mixing together graphite (including other carbons) and selected clays in proportions predetermined by experiment to produce what the pencil manufacturer calls *quality* and *degree*. The materials are mixed in water and ground in heavy mills; the quality is determined by the intensity of the grinding as much as by selection of material. The "degree" is regulated by the proportion of clay and graphite. After grinding, the mass is transferred to a specially designed filter press and subjected to hydraulic pressure, to squeeze out surplus moisture and get a close texture. The compact mass is then inserted in power-driven mechanical presses equipped with dies for the extrusion of the leads. The string-like plastic strip which exudes from the aperture of the die is laid on a board to dry. After drying, the leads are sealed in crucible boxes and fired in kilns to vitrify the clay, at a cherry-red or higher heat.

When the leads are withdrawn from the crucible boxes they are impregnated with wax by immersing them in a wax bath at an elevated temperature. The wax enters and fills the interstices between the individual particles of graphite and clay, so that in effect the pencil lead is both plasticized and lubricated. The excess of wax on its surface is carefully wiped off or otherwise removed before the lead is placed in its cedarwood "coffin."

The waxes used for plasticizing and lubricating pencil leads are preferably waxes of high melting point. Best suited for the purpose is *ouricury wax* (m. 87°C) since this wax congeals with great compactness. Although its shrinkage from molten to the solid state is phenominally great, when once hardened it has a lower coefficient of expansion than carnauba wax, and it gives sharp definition to the pencil mark. *Carnauba wax* has been used, and also *petroleum ceresins* of relatively low penetration values, and *Asiatic paraffin* of moderately high melting point. If the wax has a low softening point it may work out of the lead and loosen the glue bond between the lead and wooden coffin, causing the pencil to split. This will happen despite the usual precaution taken to remove surface wax from the lead before it is glued and encased into the pencil. Softer pencils have greater percentages of graphite and wax, which is the binder constituent, whereas the harder pencils have a greater percentage of clay and silica with correspondingly smaller percentage of graphite and wax.

The manufacture of leads for *colored pencils* is different, as the foundation consists of kaolin blended with suitable waxes and gums, which are ground together with the necessary color to obtain the hue desired. It is not a ceramic process. *Copying pencils* are made by blending graphite with aniline dye.

WAXES FOR ELECTRICAL INSULATION

A large tonnage of waxes is used in the electrical industry, mainly for insulation. Paraffine is an excellent insulator at ordinary temperatures, but for purposes where the item coated becomes heated by an electrical current or otherwise, higher melting waxes or a mixture of wax with heat-resisting material must be resorted to.

Insulating waxes are used for three principal purposes: (a) as a coating for wire, cable, or flat or irregular surfaces; (b) as an impregnant of another material, such as paper, wood, cloth, asbestos, etc., to increase its value as an insulator; and (c) as a sealing medium, that is, for potting, end-sealing, and over-all dipping, e.g., in the manufacture of capacitors. Different types of waxes are required for different purposes.

Compounds for impregnating, dipping, sealing, and potting are formulated from waxes, resins, asphalts, pitches, oils, and minerals, in which compounds there is a wide range of melting point, hardness, and other characteristics. The *impregnating compounds* are used for radio coils, transformer coils, ignition coils, wire coverings, paper tubes and forms, and for porous ceramics. *Dipping compounds* are used for coils, transformers, and condensers. *Sealing compounds* are used for condensers, batteries, switch base terminals, socket terminals, and light fixtures. *Potting compounds* are used for radio transformers, light units, loading coils, and condensers.

There is such a divergence in the products made or used by the electrical industry that the number of waxes and wax formulations employed runs into the hundreds. There are, however, certain fundamental requirements for all of the waxes so used, and these are good ductility, low shrinkage, and good insulation value.

The United States wax consumption for the electrical industry in 1951 was 29 million pounds. Of this amount 20,000,000 pounds was petroleum waxes, 5,600,000 pounds chlorinated naphthalenes, 2,200,000 pounds mineral waxes, 1,000,000 pounds special synthetic waxes, and 200,000 pounds hydrogenated castor oil.

Wax for Coating Electric Wire. An insulating wax for coating electric wires or other metal surfaces must be ductile and nonconductive of electricity, and remain so under operating conditions. It must be adhesive so that it will hold to the metal surface with tenacity, and sufficiently ductile to permit the wires to be bent without cracking the wax coating, nor must the wax crack or pull away when chilled.

Paraffin wax has the unique property of showing an increase in its insulation value with temperature rise between 25 and 35°C. In other words it has a negative temperature coefficient of electrical resistance between these temperatures before the coefficient again turns positive. Insulation waxes for coating are applied to stout electrical conductors such as cables, down to

the finest sizes of wire as in variable and fixed capacitors of 5 down to 1 microfarads capacitance.

Synthetic elastomer resins are extensively used in the more modern insulation coatings, since they have favorably low dielectric constants, for example, *polyethylene* 2.29, *polystyrene* 2.43, *"Teflon"* 2.05, *silicone* 2.90. For coating wire and cables, Happoldt and Stockfleth[78a] found that the property of extrudability of polyethylene could be greatly improved by mixing it with 5 to 15 per cent of a microcrystalline hydrocarbon wax and 0.5 to 3.0 per cent of a metallic soap, such as *zinc stearate*. It is convenient to work the polyethylene, wax, and metal salt on rolls such as are used in a rubber mill at a temperature above the melting point of the polyethylene. It should be noted that solid ethylene polymers generally have molecular weights in excess of 6000, melt at 212 to 250°F, and are very tough. The polyethylene wax-metallic soap plastic in its slab form is cut in a Ball and Jewell cutter or the like into molding powder of the desired granule size (e.g., $\frac{5}{16}$ inch).

An example of a plastic insulation composition which has been proposed for such use comprises "Polythene" (polyethylene containing 0.2 per cent antioxidant) 91 parts; microcrystalline wax (e.g., "Be Square" 170/175°F m.p.) 8 parts; and acid zinc stearate 1 part. In its application the plastic powder is fed through a Royale screw stuffer at a screw temperature of 350 to 440°F, and extruded over 20-gage single-strand copper wire at a screw speed of 20 rpm and a take-off speed of 250 feet per minute. The surface of the coated wire prepared in this manner has a thickness of 0.013 inch.

Lowden[109] enumerated the general properties of potting and sealing compounds, when used as impregnating agents for coils and other electrical equipment, as follows:

1. A viscosity which enables complete penetration to all parts at a pouring temperature of 180 to 200°C. Such a viscosity measured by the Stormer viscosimeter at 200°C can range from 100 to 500 centipoises.

2. Good adhesion to metal and to rubber or braided leads. Also to molded phenolics.

3. Excellent resistance to salt water immersion at 50°C, to water at 65°C, and to salt spray at 30 to 35°C.

4. Resistance to low temperature, −50 to −60°C, cracking under repeated cycling. If fine fractures occur, they should have an annealing tendency upon rising temperature.

5. A cold flow of at least 100°C in order to allow for an ambient plus operating temperature of 95°C maximum.

An impregnating composition comprising coumarone indene resin, *cetyl acetamide wax*, and ethyl cellulose is given in U. S. Patent 2,456,717 (1948), assigned by Lowden to Radio Corporation of America. Asphalts have long

been recognized as cheap potting compounds. Lowden[109] perfected an improved sealing composition by blending *n*-butyl methacrylate and *cetyl acetamide wax* with asphalt. For example, a blend giving a viscosity of 165 centipoises, a B & R softening point of 120°C, and a cold flow of 98°C may be prepared from low-melting asphalt 90 parts, cetyl acetamide wax (m. 137–139°C) 6 parts and normal butyl methacrylate polymer having a softening point of 65.5 to 74°C.

Where asphalt is not a component in the cetyl acetamide compositions, a stabilizer and mineral filler (mica, silica, "Fiberglas," etc.) may be beneficially used in potting waxes.

Dielectric Measurements. The "dielectric strength" of an insulating material is the maximum voltage that unit thickness can withstand without rupture. The two electrical properties most commonly quoted are dielectric constant (K) and power factor (PF). K is the ratio of the capacity of a condenser to the capacity of the same condenser if the dielectric were a vacuum. Since the dielectric constant of air is a mere trifle higher than for a vacuum, K for air can be considered as unity, sufficiently accurate for most measurements. For details of the ways and means of measuring K, PF, and other dielectric measurements consult ASTM *Standards*, 1946, Part III B, Non-Metallic Materials: Nos. D 149-44; D 150-46 T; D 237-46; D 495-42.

The plastic insulation composition comprising polyethylene, microcrystalline wax, and acid zinc stearate, as above described, has a K value of 231 and PF of 0.00006, both at 1000 cycles; and a K value of 2.11 and PF of 0.00104 at 1,000,000 cycles, both at 25°C, which makes the composition suitable for use at radio frequencies.

The value (KV) obtained for the dielectric strength of a specimen of wax will depend on such factors as the type of voltage (d-c or a-c), frequency, duration of application, rate of rise, temperature, humidity, shape, size of electrodes, and the nature of the surrounding material. Metallic electrodes are applied to the dielectric and the maximum voltage gradient varies inversely with the radius of the electrode and becomes more uniform as the area of the electrodes in the condenser is increased. The a-c instruments customarily used operate at various frequencies, namely below 10^8 ~/sec, or 10^8 to 10^{10} ~/sec, and the resulting K value is noticeably higher for the lower frequency when the wax specimen contains moisture.

Potting Compounds. When the components of a miniature or subminiature electrical or electromechanical device, instrument, or assembly are fully imbedded in a plastic substance, the material thus used is termed a potting compound. Plastic materials include polyesters and modified styrene, desirable for their good dielectric characteristics and specific inductance capacities. Modified asphalts, phenolics, silicones, and eth-

oxylines are also used. Nitro waxes, amide waxes, paraffin wax, chlorinated waxes, carnauba wax, montan wax, shellac wax, and microcrystalline waxes have been considered for potting purposes. By extending their melting points with cellulose derivatives, synthetic resins, and polyethylene waxes, the value of the wax materials is enhanced. Generally speaking a potting wax is a mixture of waxes, or wax and resin.

According to Delmonte[45a], characteristics required of a potting compound include (a) optimum resistance to water and water vapor, (b) resistance to dislocation due to shock, (c) satisfactory heat dissipation, (d) minimum leakage of electric current, (e) resistance to chemical fumes, (f) ability to flow and imbed components, (g) minimum shrinkage, (h) adhesion to container walls.

To exclude moisture or moisture vapor the potting compound must make an effective hermetic seal. An outstanding example of shock is that of the electronic gear and recording apparatus expelled from V-2 rockets after test firing. Many electrical and electronic devices give off heat during operation. If this heat is allowed to accumulate in a dead air space, the temperature may rise to an undesirable degree. The potting compound must dissipate the heat, and yet be of low thermal conductivity so that cooling effect is minimized. It should have good surface insulation resistance to minimize leakage of electrical currents.

Radio Condensers. Radio condensers require waxes of a more exacting specification than do stout electrical conductors or the ordinary size wire. For example, the condenser in the small radio set in service becomes readily heated, therefore necessitating the use of a wax that will withstand at least 160°F of heat without softening or partially melting. Miniature assemblies require even higher melting point waxes. Waxes such as *shellac wax*, *esparto wax*, *candelilla wax*, and *fiber wax*, when plasticized by an adequate amount of a softer wax of high melting point, are suited for the purpose. A softer wax would be a *microcrystalline wax* of 170/175°F m.p. with a relatively high penetration value. The large coefficient of expansion of *carnauba wax*, and certain other hard waxes, makes their use for insulation rather undesirable. Microcrystalline waxes to which elastomer resin or pitch has been incorporated, thus yielding a wax of over 200°F melting point, are supplanting to a considerable extent the natural plant waxes as insulating mediums. The addition of polyethylene wax (m. 207–223°F) in a small amount to *microcrystalline wax*, and proportioned with a substantial amount of shellac wax, provides an insulation wax which has an excellent dielectric strength, shows but little shrinkage, and which will withstand high temperatures without softening.

Microcrystalline waxes, inclusive of blended compositions, have been found useful in the electrical industry for impregnating radio condensers

and capacitors; for coating all types of coils; for impregnating fabric and paper covering for copper wires, cables, etc.; as an ingredient in potting compounds for waterproofing of ceramic insulators; and as an insulating cement for porcelain insulator units.

The dielectric constants (K, of electrostatic system) given for glasses are 5.83–9.90, mica 8, paraffin and other waxes 1.96–4.50, rubber 2.5, shellac 2.95–3.73, ebonite 2.21–3.21, sulfur 2.88–3.84, polyethylene 2.3–2.5, petroleum 2.02–2.07, benzene 2.36, ether 4.2–4.4, gases (about) 1, vacuum 0.9995, water 76, and alcohol 26.

The Lowden impregnating composition of coumarone indene resin, cetyl acetamide, and ethyl cellulose is of a very light brown color, very flexible, and somewhat tacky. Its density is 1.07 at 25°C. The flash point is 238°C and fire point 296°C. The ball and ring softening point is 118–121°C. The dielectric constant is 2.5 at 25°C at a frequency of 1 megacycle. Coils impregnated with the compound exhibit no cracking at −55°C and no drift at 115°C.

A potting compound of high dielectric strength, and superior flowing properties to the wax-resin, or wax-polyethylene compounds, was prepared by Warth, Jr.[171] This compound was prepared from *shellac wax* 30, *microcrystalline wax* (170°F m.p.) 60, and *polyethylene wax* (m. 97–106°C) 10 parts. The blended wax has a melting point of 96.7°C (206°F), and a penetration value (100 g 5 sec 25°C) of 10.5°. It is resistant to moisture vapor, very cohesive, of good tensile strength, and retains its flexibility at very low temperatures. A potting compound which will withstand a temperature of 105 to 115°C (221–239°F) may be prepared from *shellac wax* 28, *microcrystalline wax* (170°F m.p.) 61, and *polyethylene wax* 11 parts.

Capsulation of amplifiers and oscillator subassemblies is effected by means of a casting resin. Newly developed hearing aids employ condenser and resistor network assemblies embedded on a polyester resin. Electronic miniaturization and subminiaturization projects have developed rapidly in the American national defense activities.

De Coste[32b] of Bell Telephone Laboratories, Inc., patented a compound for use in sealing insulated electrical conductors, which is a mixture of a polymerized olefin, hydrogenated rosin, and amide wax. A typical mixture contains polybutene (mol. wt. about 5000) 65.5, hydrogenated rosin 30.0, condensate of long-chain fatty acid with alkyl polyamine 4.0, and antioxidant 0.5 parts by weight. The amide wax has a powerful gelling action, and the function of the hydrogenated rosin is to prevent premature gelling. The mixture is resistant to flow up to about 100°C.

Sealing Waxes. A fire-resistant putty composition useful for the sealing of electrical apparatus can be prepared according to the formulation of Dodd[47a], namely, chloronaphthalene (54% Cl) 29.1, chlorinated paraffin wax

(53% Cl) 9.0, oleic acid 6.5, petrolatum jelly 5.2, slaked lime 3.2, hexachlorethane 1.3, and china clay 45.7 parts. The wax and other ingredients are combined together with the aid of heat and in the order named. The lime reacts with the oleic acid, and the china clay is added last to the melt with stirring. The mass is allowed to cool, and masticated on rolls to a completely homogenous paste or putty, which can be colored if desired.

"Kleiderer's sealing composition" is composed of ethyl cellulose 20–30, hydrogenated castor oil 35–40, paraffin wax 35–40, and hydroquinone monobenzyl ether 0.5–2, parts. [Kleiderer, C. W. (to the U. S. of America), U. S. Patent 2,599,762 (1952)].

Melted wax is sometimes mixed with a polymerizable insulating liquid such as polystyrene, acrylic and metacrylic esters. After forming into suitable shape, or applying as coating, or the impregnation of parts to be insulated, the mixture is polymerized, with or without pressure and at high temperature. ["Hermes," Belgian Patent 447,902 (1942)].

Telephone Switchboard Wire Insulation. Wire for indoor use, such as for telephone switchboards and exchanges, is covered with fibrous material. To protect the material, whether textile, paper, or paper-pulp, from moisture absorption, it is covered with a synthetic linear condensation polymer which may be cold drawn without the use of a solvent. The polymer is of high molecular weight, such as polyethylene sebacate, softening at 72°C and forming a viscous melt at 130°C. With a softening point above 60°C the coating is heat-resistant at ordinary temperature. The polymer can be used with a solvent, such as biphenyl (m. 71°C) or β-naphthol (m. 122°C) if the fabric is to be impregnated. The polymer in its melted form furnishes a protective coating for rubber insulated conductors and is of special use on telephone wires exposed to abrasion and shearing stress of outdoor wiring. [Fuller, C. S., U. S. Patents 2,349,951 and 2,349,952 (1944)].

Wax for Coating Cables. An insulation wax for cables, i.e., *cable wax*, differs somewhat from that for electrical wires. Cable wax should have a melting point of 55 to 65°C, and must not be sticky. It must be resistant to steam and to weak alkalies and acids, and inexpensive. *Ozocerite wax* conforms to these requirements except that it is too expensive. Mixtures of *montan wax* and *paraffin* have been used in Germany. Montan cable wax AA has a saponification number of 15.0 to 15.7, is of good dielectric strength, and has a high breakdown voltage.

Diggs *et al.*[46] were probably the first to find a petrolatum wax suitable for the purpose. This type of microcrystalline wax was prepared from Salt Lake crude oil and contained somewhat over 15 per cent occluded oil; it melted at 160°F, and showed a breakdown test (BDV) in liquid state of "O.K. at 25,000 volts."

An electric cable insulating composition of the Pirelli-General Cable

Works, Ltd.[134], in England is made from an elastomer resin, such as polyethylene, and petrolatum; or polyethylene incorporated in a mixture of petroleum oil with paraffin wax, in such proportions as to make it a simple task to impregnate the cable dielectric composition at a temperature up to 80°C (176°F). Petrolatum wax, which contains somewhat over 15 per cent of occluded oil, melts at about 71°C (160°F) and shows a BDV test in liquid state of O.K. at 25,000 volts.

The dielectric strength (*KV*) of a wax varies with temperature. For example, a microcrystalline wax [165/170°F (ASTM)] has a dielectric strength of 50 at 30°C (86°F), of 31 to 38 at 70°C (158°F), and of 35 to 41 volts per mil at 100°C (212°F).

In electrical power cable installations requiring vertical risers, such as in mine shafts, the migration of the penetrating oil toward the lower sections is deterred by the replacement of all or part of the oil by *microcrystalline petroleum wax* having a melting point of about 80°C (176°F). King advises that not less than 55 per cent of the impregnant be microcrystalline wax. To improve the low-temperature properties it is proposed that the balance of the composition consist of oil and plasticizer. The plasticizer is a mixture of polyisobutene (mol. wt. 20,000 to 100,000) and rosin. Complete impregnation has been obtained with these compounds at a temperature of 130°C (266°F). At 0°C these materials are sufficiently plastic to allow some sliding of the papers without damage as the finished cable is handled. [King, A. U. S. Patent 2,586,345 (1952)].

Wax for Electric Condensers. An electric condenser usually consists of metallic plates separated and insulated from each other, e.g., sheets of aluminum foil and wax paper. The amount of electricity that can be stored in the condenser depends upon the voltage, the size of the plates, their distance apart, and the nature of the insulator separating them. With higher voltage and larger plates more electricity can be stored in the condenser; and this ability to store electricity is measured by its *capacitance*. Capacitance is the important feature and not ohmic resistance. In condensers employed in electronic circuits the insulators between the plates are mica, hard rubber, waxed paper, air, etc. The dielectric constant or specific inductive capacity of the material used as insulator between the plates or electrodes functions in direct proportion to the capacitance. Therefore, beeswax, which has a dielectric constant of 3.2, will not produce as high a capacitance as mica which rates at 5.6 to 6.4, though slightly better than ebonite which rates at 2.5 to 3.0. The unit (1.0) is the dielectric constant for air.

It is obvious that if a condenser of high capacity is to serve in a small space, a wax with a high dielectric constant must be chosen, with due regard also to the amount of voltage that can be impressed across dielectric, so as to avoid its breakdown. Electric condensers in the small sizes may be (a)

wax paper condensers, or (b) *electrolytic condensers*. The *paper tubular condenser*, used so widely in radio circuits and in many types of electronic equipment, contains much wax. The *capacitor* in the paper condenser is composed of alternate sheets of very thin foil and wax paper; the pile is rolled into a small cylinder, e.g., 1 cm diameter x 2.5 cm long and placed in a wax-impregnated tube with its wire terminals protruding. Each end is then filled with wax, termed *end-fill wax*, i.e., a wax that will pour well at an elevated temperature, that will not interfere with the impregnating material in the capacitor, and that will be resistant to all possible climatic conditions to which the condensers are exposed. The complete assembly is given an overall dip in another wax, e.g., paraffin and microcrystalline wax, to improve its moistureproofiness.

The impregnating material of the capacitor is generally "*Halowax*," but any wax having a high dielectric constant, low power factor, and good chemical resistance can be used. The *end-fill wax* is usually a mixture of wax, a resin that will flow as freely as water when heated ("Aroclor"), and a filler such as powdered mica. The *overall-dip wax* is the same as the wax used for the tube impregnation, such as microcrystalline petroleum wax of pale color and high melting point. An example of a tiny condenser used in a small electronic unit is one that only measures 150 mm in length by 25 mm in diameter, stamped with the rating "2000 ohms, and 20 Q" on the outside, and further identified by its red color for that size.

Electrolytic condensers are in a sense chemical condensers. There are hundreds of different kinds, some of which have liquid electrolytes and others solid. In general they depend upon the difference in electrical potential between the elements used in their make-up. A liquid condenser might be crystals of citric acid and glycerol; a solid one, wire electrodes insulated by a porous material impregnated with the electrolyte; or layers of foil and cambric folded zigzag and impregnated with sodium borate; or simply plates of metal with a layer of oxide. Electrolytic condensers are usually of larger size, ($1\frac{1}{2}$ to $1\frac{1}{2}$ inches in diameter) than the wax paper condensers. The casing is generally a molded plastic which has been wax-impregnated in vacuum before assembly. When paper tubes are used to house the electrolytic elements the former must be moistureproofed with wax in the same way as the paper tubular condensers. In some instances insulators are made of porcelain. A free-flowing wax-resin mixture is used in the construction of the capacitor element, which itself is potted in the casing with pitch.

Battery Separators. Storage batteries which are in a series, such as those in a submarine, are separated by barriers of wax, preferably a wax of good tensile strength such as paraffine to which has been added 20 to 30 per cent of microcrystalline wax.

Electroplating Waxes. Waxes are of considerable importance in the

art of electroplating, particularly when the object is to be produced in two or more metallic colors (such as nickel and brass) by electroplating, or the design is to be shown in both matte and bright areas. Wax is used as a "stop-off" for the electrolytic deposition of the metal or alloy in the affected area. It is also used in insulating the rack which holds the work, particularly where the work hung on the rack is made the anode for electropolishing; and deposition of metal on the rack is to be avoided while using the chemicals such as phosphates, borates, etc., as special electrolytes. A petroleum ceresin of 175/185°F melting point is of considerable value to the electroplater, although other high-melting flexible waxes are also used.

Ratings for Insulation Waxes. Waxes for electrical insulation purposes are generally rated according to following constants:

(1) Water absorption
(2) Dielectric strength at 60 cycles
(3) Power and loss factors at 1000 kilocycles, with dielectric constant
(4) Melting point

A wax to be of value as an electrical insulator must show no water absorption when subjected to treatment with distilled water for 24 hours. Water absorption is then expressed as 0 per cent. The dielectric strength at 60 cycles is determined by ASTM Method D 149-40 T. For example, a wax may show an average of 62.6 kilovolts at puncture for an average thickness of 131 mils. Then the average dielectric strength would be 62,600 ÷ 131, or 470 volts per mil. A specimen of a synthetic wax had a power factor at 1000 kilocycles of 0.002; a loss factor at 1000 kilocycles of 0.004; and a dielectric constant of 2.20; according to ASTM Method D 150-41 T.

The electrical data are always considered in conjunction with the chemical data, e.g., melting point, saponification number, acid value, ester value, and specific gravity at 25°C.

Dielectric Constants of Waxes. Lee and Lowry[104], of the Bell Telephone Laboratories, in 1927 reported their studies of the dielectric constants of insulating waxes, resins, and bitumens, and the effect of moisture on such substances.

The following substances have a dielectric constant in the initial dry stage within the limits indicated:

2.0–2.25 Paraffin
2.25–2.5 Candelilla wax, ceresin, ozocerite, paraffin, stearic acid, "Superla Wax."
2.5–2.75 Montan wax, montan pitch, rosin, aluminum stearate, zinc stearate.
2.75–3.0 Carnauba wax, Chinese insect wax, coumarone-indene resin, japanwax, beeswax.
3.0 3.25 Bayberry wax, manila copal, petroleum asphalt.

3.25–3.5 Stearin pitch

3.5–3.75 Paraffin-beeswax compound, spermaceti, shellac, "Halowax"

Dielectric constant not increasing more than 0.3 on six months' immersion test in 3.5 per cent NaCl solution:

Asphalt, beeswax, ceresin wax, coumarone-indene resin, japanwax, montan pitch, montan wax, ozocerite, manila copal, paraffin, rosin, stearin pitch, "Superla Wax."

Dielectric constant greatly increased after immersion:

Aluminum stearate to over 4.9, bayberry wax to 10.4, carnauba wax to over 3.8, Chinese insect wax to over 3.6, "Halowax" to over 4.2, shellac to over 7.7, spermaceti to over 6, shellac to over 7.7

All the waxes, and other materials tested, responded well to redrying, the dielectrical constants being restored to about as low or lower than the original dry ones.

Lee and Lowry also tabulated the "Effective A-C Conductivity" (Unit = 10^{-12} mho cm), initial, after immersion, and final (after redrying). They also tabulated the "Volume Resistivity" (Unit = 10^{13} ohm-cm). A considerable amount of water is absorbed by some of the waxes. The natural waxes which contain fatty acids and esters absorb more water than the hydrocarbon waxes. Shellac, which is widely used as an insulating material in electrical apparatus, absorbs 4.3 to 5.1 per cent of water and loses its insulating properties to an appreciable extent.

The dielectric constant for the various grades of polyethylene waxes is 2.5 (60×10^6 cycles); that of a microcrystalline wax in the range of 2.5 to 2.75.

Microbiological Failures with Hydrocarbon Waxes

The bacterial decomposition of the paraffin hydrocarbons of petroleum and ozocerite yields a peculiar substance, closely related to hydrocarbons and proteins, which is known as "algarite," and regarded as a product of the later phases of geochemical history of petroleum. Decomposition of algarite by bacteria results in the formation of methane.

The failure of underground pipelines or electrical conduits "protected" from corrosion by paraffin-impregnated material may be attributed in part to the activities of microorganisms which decompose hydrocarbons. Thin layers of paraffin are penetrated by *Botrytis cinerea*, and 17 other species of soil bacteria. It has been found that the soil mold *Penicillium glaucum* can utilize paraffin as the sole source of energy. *Bacterium aliphaticum* will grow on a sterile inorganic nutrient salt solution to which, as the only source of carbon, has been added melene in finely divided form. *Bacterium aliphaticum liquefaciens* is active on hydrocarbons ranging from *n*-hexane to tetratriacontane, $C_{34}H_{70}$, and some of the cyclic hydrocarbons as well.

Growths can take place with *Micrococcus paraffinae*, *Mycobacterium album*, and *Mycobacterium rubrum*, which will consume appreciable amounts of paraffin. The mold *Aspergillus versicolor* assimilates the hydrocarbon *n*-tricosane, $C_{23}H_{48}$, very well, but will not assimilate the larger molecule *n*-pentatriacontane, $C_{35}H_{72}$. Paraffin wax of 45°C melting point was found to provide growth of soil fungi and bacteria better than 55°C melting point. The reader is referred to "Action of Microörganisms on Hydrocarbons." [*Bact. Reviews*, **10**, 1–49 (1946), 182 references.]

WAX FOR EXPLOSIVES AND PYROTECHNICS

Wax of some description is occasionally an ingredient in an explosive composition, but more often constitutes the waterproofing agent for the explosive wrap. Fully refined *paraffines*, and to a lesser extent mixtures of paraffine with *microcrystalline wax*, are the waxes generally used for such purposes.

Gunpowders. The gunpowder manufactured in the United States is known as "A" or "B" blasting powder. These powders come in a variety of granulations. The "A" is used for black sporting powders, for making safety fuse, for pyrotechnics, and for quarrying dimensional stone. It is a mixture in suitable proportions of potassium nitrate, charcoal, and sulfur. The "B" is made from the cheaper sodium nitrate, is of lower strength, and is used mostly in mining coal. Granulated powder is also compressed into cylindrical pellets with a central perforation. These powder pellets are wrapped in a waxed cartridge paper, and fired by a fuse.

Dynamites. The majority of dynamites consist of nitroglycerin, which is a liquid, admixed with an absorbent of sodium nitrate and wood meal. Straight nitroglycerin dynamites are made in strengths of from 15 to 60 per cent liquid nitroglycerine. They have a relatively high rate of detonation, and therefore, are used wherever a quick action or a shattering effect is desired. Nitrostarch is also used in place of nitroglycerin, where it is necessary to have a nonfreezing dynamite. The various types of dynamite are nitroglycerin, nitrogelatin, gelatin, ammonia gelatin, blasting gelatin, etc. All dynamite (except in large diameters) is packed in cartridge form by large, semiautomatic machines. The explosive charge is wrapped in paper, the ends of which are folded in, and the resulting cartridge is coated with *paraffin wax*.

According to Sorenson[155], an explosive suitable for blasting can be made from ammonium nitrate 100, manganese dioxide 15, *paraffin wax* 6, petroleum naphtha 6, rosin 15, potato flour 8, aluminum 30, and nitroglycerin 100 parts. Burrows[22] specified a mixture of barium nitrate 32, dinitrotoluene 10, coarse aluminum 7.5, fine aluminum 0.5 parts, with or without the addition of charcoal and *paraffin wax*.

"Amberite." "Amberite," manufactured by Curtis and Harvey, Tonbridge, England, contains according to its assay the following ingredients: guncotton 13, colloidal cotton 59.5, barium nitrate 19.5, a little potassium nitrate, *paraffin wax* 6, and volatile matter 2 parts. It is essentially a nitrocellulose powder.

Mining Powders. Palmer[127] specified a mining powder, claimed to be nonhygroscopic, powerful, and rapid, consisting of ammonium perchlorate 50, dinitrotoluene 14, sodium or potassium 31, aluminum powder 5, and *paraffin wax* 5 parts.

Rocket Propellants. Solid-propellant rockets are used in bazookas, gun projectiles, assist-take-off units for airplanes, and boosters and sustainers for other large rockets and guided missiles, and are nearly always "single trip" units. The grain composition and design are important factors in the specified "burning time." In the composition of so-called "double-base" solid propellants a very small amount of wax may be used, more particularly *candelilla wax*. The chief ingredients customarily are nitrocellulose and nitroglycerin.

Wrappers for Explosives. The wrapper of the explosive forms a part of the chemical mixture in the reactions that occur on the detonation of the explosive; this is a factor which is taken into consideration in the formulation of dynamites of all types. A small additional percentage of sodium nitrate is used in the explosive formula so that the entry of the paper and *paraffin* of the wrapper into the reaction will not too greatly increase the amount of carbon monoxide (CO) produced on explosion[101a].

Mining and Quarrying Explosives. Straight dynamites (nitroglycerine base) have been largely supplanted by "ammonia dynamites" and "ammonia gelatin dynamites" for mining and quarrying explosives. In ammonia dynamites roughly half of the nitroglycerin is replaced by a somewhat increased amount of ammonium nitrate, thereby reducing the cost. For example, a 40 per cent ammonia dynamite may be prepared from nitroglycerin 16.5, sulfur 3.6, ammonium nitrate 31.4, sodium nitrate 37.5, antacid 1.1, and carbonaceous combustible material (inclusive of any paraffin) 9.2 parts.

Ammonia gelatin dynamites, graded as 30 to 80 per cent, contain moisture 1.5–1.8 per cent, nitroglycerin 23–28 per cent, nitrocellulose (soluble) 0.3–0.9 per cent, sulfur 3.4–7.2 per cent, ammonium nitrate 4–33 per cent, sodium nitrate 15 to 55 per cent, antacid 0.7–0.9 per cent, and carbonaceous combustible material 4.3–8.3 per cent[101a]. Wax is seldom used in dynamite compositions. A milder and slower (phlegmatized) form of dynamite known as dynamite No. 2 does contain *paraffin wax*, and consists of nitroglycerine 18, uniformly mixed with potassium nitrate 71, charcoal 10, and *paraffin wax* 1 part.

Sensitizers for Ammonia Nitrate Explosives. Of the various kinds of effective sensitizers used for ammonium nitrate explosive are the paraffin oils and waxes. One type of ammonia nitrate explosive employs an amount of sensitizer insufficient to make the explosive capable of detonation from the action of an ordinary blasting cap, although it may be detonated by a materially heavier initiating charge. By the use of heavy "booster charges" (usually TNT or "Amatol") these explosives of low sensitivity can be caused to detonate completely. Such explosives are much safer to handle. A typical composition would be ammonium nitrate 92.5, dinitrotoluene 4.0, and *paraffin wax* 3.5 parts. The velocity is generally between 3500 and 5000 meters per second[100a].

Wax in Blasting Composition. Gelatine dynamite consists of a colloidal solution of guncotton in nitroglycerin, absorbed in a mixture of sodium nitrate and wood meal, whereas the normal dynamites contain no guncotton. Blasting gelatin consists of nitroglycerin in which has been dissolved nitrocotton to form a jelly, together with a small proportion of antacid, such as chalk, but contains no wax. The plastic consistency of this explosive allows it to be extruded through a nipple of the required diameter into *paraffin-paper shells* to form cartridges. Blasting gelatin is the strongest and one of the quickest explosives manufactured for commercial use, and the wrapped cartridges are paraffined.

The stick dynamite is paraffined to obtain maximum moisture protection and rigidity. Gelatine dynamite is used for wet work and under water blasting. Pearsall[129] found that many advantages are gained by directly coating the cartridge with wax of a high melting point and dispensing with the paper wrap which often proves a source of trouble. *Microcrystalline wax* serves the purpose well when used as a protective coating. The application of the wax can be taken care of by dipping the cartridge in the melted wax, or by other suitable means.

Cartridge Paper. This designation is given to (a) manila wrapping paper, 50 to 80 pound per ream basis weight, sometimes waxed on one side, and used as containers for dynamite or other explosive material; or to (b) a three-ply paper, produced in a particular manner and use to make short gun shells.

Cordite. Cordite, the English Service propellant (produced in cords) is essentially a mixture of nitroglycerin and guncotton, thoroughly incorporated and gelatinized by means of acetone. "Vaseline," or crude mineral jelly, is used to stabilize it, to prevent it from fouling magazine rifles by the bullets, and as a waterproofing agent. Cordite does not ignite readily, but when once ignited it burns slowly with a strong yellowish flame, which is practically smokeless. Cordite is insensitive to shock, and burns explosively only when strongly confined. The ballistic power of cordite

is four times that of black powder. The color of cordite varies from light to dark brown, according to the color of the mineral jelly used.

Cooling Agent for Smokeless Powder. Most smokeless powders have a high temperature of explosion, which not only causes erosion of the bore of the gun but also gives a strong and readily visible flame. To produce a flameless explosive Luciani[109a] proposes the addition of a mixture of *carnauba wax*, *beeswax*, and sodium bicarbonate to the smokeless powder.

Safety Explosives. A safety explosive manufactured by Curtis and Harvey, Tonbridge, England, is known as "Bobbinite." It is really a high-grade gunpowder containing but little sulfur, with ingredients added to increase its safety. As originally made, according to Thorpe, it consisted of niter 64, sulfur 2, charcoal 19, and a mixture of ammonium sulfate and copper sulfate 15 parts. The sulfates were later replaced by starch 8, and *paraffin wax* 3 parts, other constituents being correspondingly increased. The mixture is compressed into pellets, which are then coated with paraffin wax. "Bobbinite" is safe to handle and is fired without detonators; it is slow burning and not dangerous in fiery mines.

Shell Powder. Shell powder may be prepared, according to Bowen[17], from ammonium perchlorate 75, aluminum powder 12, and *paraffine* 13 parts. The powder matte if extruded through bronze dies requires *candelilla wax* or its equivalent to lubricate the dies.

Fuses and Detonators. Wax emulsions having *carnauba wax* as the principal wax constituent are used for waterproofing fuses and detonators. The same emulsion is used in waterproofing powder bags in the Navy. Yellow amorphoid hydrocarbon waxes of 160–165°C melting point are also said to find an extensive use for such purposes. *White bleached beeswax* is employed to some extent.

TNT Explosive. Burrows and Burrows[21] prepared an explosive consisting of a mixture of ammonium perchlorate 6, potassium nitrate 56, aluminum 18, and trinitrotoluene 18 parts, to which they further added 2 parts of refined *paraffin wax*. The aluminum is prepared by pouring the molten metal on a rapidly revolving wheel which dashes it in a spray into cold water, thus producing large particles with sharp points susceptible to rapid ignition. The α- or 2,3,4-trinitrotoluene is that obtained by the distillation of the so-called liquid trinitrotoluene and is known as "tolite," "trilite," "trinol," and "trotyl."

Wax-coated Explosive Particles. Particles of an explosive composition may be coated with wax, to render them safe for handling, by treating the particles in aqueous suspension with a waxy substance in the presence of a surface-active agent. The waxy substance should not exceed 2.5 per cent by weight of the powder so treated. For example, particles of trinitrophenylmethylnitramine (100 g) are suspended in water (200 g); after heat-

ing to 98°C with stirring, ricinoleic acid (0.02 g) is added as surface-acting agent, followed by molten paraffin wax (0.9 g). The yellow press cake obtained following cooling and filtering is dried in the air at 40°C, after which the material may be pelleted. The pellets are smooth and compact and do not contaminate the skin on handling. [Baron, C. E. H., and Imperial Chemical Industries, Ltd., British Patent 585,916 (1947)].

Phlegmatizing Wax for Explosives. A wax of a suitable kind is incorporated with an explosive material when it is desired to reduce the speed of explosion. Its customary function is to provide a less intimate contact of the particles of the explosive with one another. *Phlegmatizing waxes* may be roughly classed as A, oxygen-containing, such as fatty esters and ketones; and B, nonoxygen-containing, such as paraffin and ceresin. An instance can arise where a wax of class B is not compatible with the explosive material, necessitating the use of a wax of class A, as in phlegmatizing tetranitropentaerythritol; or on the other hand there are cases where A is undesirable because of its oxygen content, and the use of B is advantageous because of the release upon firing of hydrogen atoms, which function as the slowing barrier. *Paraffin wax* is known to act as an agent for absorbing neutrons, and is used for protecting personnel working on atomic energy research. Phlegmatizing waxes are also occasionally used in pryotechnic material.

In World War II, the Germany military employed a phlegmatizing wax in their tetranitropentaerythritol and R.D.X. explosives for their African campaign. A suitable wax was found in a ketone of 90°C melting point obtained by heating together a mild oxidation product of montan wax, and a long-chain synthetic hydrocarbon which had been partially converted to a wax acid by the Fischer-Tropsch process, with the aid of a potassium permanganate catalyst. In the latter process the oxidation was stopped when the acid value reached 40 to 45, and the melting point about 80°C. The waxes that were fused together to prepare the ketone were the equivalent of what is now known as "Gersthofen L" and "Gersthofen Wax S."

Paper Shot Shell Tubes. These shell tubes are impregnated with *paraffin wax*. Schilling and Latham, Remington Arms Company[144] claim that if the paraffin wax is kept at the impregnating temperature, 230 to 240°F (110–115.5°C) in a tank for an extended period, acidic decomposition products are formed, and their presence not only interferes with the proper penetration of the wax into the paper tubes, but thereby decreases the resistance of the paper tube to burning powder. If the powder burns through the tube, failure of the tube will result, and upon extraction of the fired shell from the gun, a part of the tube will be left in the barrel. The degree of the decomposition may be measured by determining the saponification of the wax. The decomposition of the paraffin can be arrested by the addi-

tion of a small amount of polyalkylated phenols; e.g., 2,6-dimethyl and 2,4,6-trimethyl phenol.

It was found that if a *crude scale paraffin wax* was heated for 72, 141, and 230 hours, the saponification values were 10.0, 14.0, and 29.0 respectively. By adding 0.50 per cent of the inhibitor to the paraffin to begin with, these values came down to 0, 0, and 0.5 respectively. A standard practice is to keep the saponification values below 10 or 12. This can be accomplished by adding fresh wax to the tank at frequent intervals, but it is a simpler matter to use an inhibitor. To be effective the quantity added should be at least 0.2 per cent.

Cartridge Cases. In the preparation of cartridges having metal cases, it has been found desirable (according to Pedersen[131], of Springfield, Mass.) to apply to the metal case a relatively thin coating of some protective substance which will preserve the metal case for comparatively long periods of time against deterioration, such as seasonal cracking. It is also desirable to choose a coating which will perform the additional function of acting as a lubricant for the case of the cartridge, for facilitating introduction into the chamber of the gun and extraction thereof after firing.

The most suitable wax found for waxing metal cartridge cases according to Pedersen is *ceresin*, a refined product of ozocerite. This is because of the hard and nontacky properties of ceresin at ordinary temperatures, and its melting point range between 140 and 176°F. It is smooth and glassy when hard and does not gather dirt or dust. When the ceresin on the cartridges is melted in the chamber of a gun, it becomes a lubricant.

In applying the wax to the batch of cartridges, it is desirable to preheat the cartridge cases to approximately the same temperature as that of the heated bath of the wax solution, in order to secure a uniformly thin film, and to accelerate the drying or evaporation of the solvent. The latent heat in the cartridge case, because of the preheating, is effective in drying out the coating film and speeding up the waxing operation as a whole.

In the Pedersen process about 7 per cent of *ceresin* is dissolved in carbon tetrachloride, and the solution is then heated to approximately 100 to 120°F. The cartridges are likewise heated to the same temperature so that there will be no heat exchange in the application whether by dipping, spraying, or brushing. The dipping process is preferred. The process can be made a continuous one in which the cartridge cases pass on a conveyor through a drying oven, into the heated liquid bath and out through a current of heated air to vaporize the solvent. Instead of ceresin (ozocerite) a *petroleum ceresin wax* can be used.

Pyrotechnics. Pyrotechnics are fireworks which may be classed as (a) military or (b) commercial. Military pyrotechnics are employed primarily for either illumination or signaling, and have been instruments of warfare

for centuries. Commercial pyrotechnics such as rockets, Roman candles, etc. are firework displays which were well known in China for many centuries, prior to their introduction in Europe.

The constituents employed in pyrotechnic compositions comprise oxidizing agents, fuels, color intensifiers, retardants, binding agents, and waterproofing agents. The oxidizing agents used are nitrates, perchlorates, peroxides, oxides, chromates, and chlorates. The fuels are selected from a number of finely divided metals, phosphorus, charcoal, sulfur, etc. The color intensifiers are usually organic chlorine compounds, such as polyvinyl chloride, etc. The retardants used are of many kinds, including *paraffin waxes*. The binding agents are many kinds but include waxes. The waterproofing agents also include waxes.

Commercial pyrotechnics are made largely to satisfy use demands, such as ceremonial or industrial. Chinese firecrackers are sound pyrotechnics. Railway signal torpedoes, etc., are for industrial use. Pyrotechnic compositions used to make color usually contain chlorates or nitrates, although chlorates should never be used in conjunction with ammonium salts as the mixture can turn out to be highly explosive. The fuels and binders may include petrolatum and stearic acid. In some instances, such as the fuses for blue fire, *paraffin wax* is used with potassium chlorate as the combustible substance.

For white lights the following composition may be used: barium nitrate 30–40, strontium nitrate 6–8, magnesium 50–54, and *paraffin wax* 2–4 parts. Color flame effects can be obtained from barium nitrate and particles of a magnesium or aluminum bronze alloy with 1 per cent of liquid wax. A signal torch or flare has been made from strontium and potassium salts, lacquer, sulfur, sawdust, *petrolatum*, and *paraffin* wax.

Wax as a whole has a very limited use in pyrotechny other than in waterproofing the cartons in which the fireworks are shipped.

WAXES FOR FLOORS AND FLOOR COVERINGS

The floor being the integral part of the interior of a building which must withstand most of the wear, it is logical that it should receive especial attention and care. The application of waxes to wooden floors, such as parquet floors, for the purpose of their preservation, dates back centuries. Many floors are covered with a soft pliable material, such as linoleum, rubber tile, congoleum, and plastic, which is cemented or otherwise fixed to the original flooring. Quite often a layer of felt is laid between the under flooring and the floor covering to act as a cushion. The application of wax to such flooring material retards the penetration of air and moisture, thereby increasing the life of the cushioning material as well as preventing deterioration of the surface by abrasion from grit.

Wood floors should have a foundation coat of paste wax after a thorough cleaning, although subsequent waxing may be carried out with a liquid floor polish, in which the solvent is of a type that will tend to cleanse as well as leave a film of wax which may be rubbed to a high luster. Paste waxes are preferred where power machines are used on the floors. A paste wax is semi-solid at ordinary room temperatures and contains about 30 per cent of nonvolatile matter. The solvent may be the same as that used in liquid waxes. Liquid waxes are generally preferred to paste waxes for polishing floor coverings.

Classification of Floor Waxes. Floor waxes may be classified, for convenience, in the following manner:

(1) Solid floor waxes:
    (a) In paste form
    (b) In powdered form
(2) Liquid floor polishes:
    (a) Rubbing polish
    (b) Nonrubbing polish
    (c) Mop oil

Floor waxes are mixtures of waxes of various degrees of hardness with a suitable solvent or dispersing agent, with or without the addition of resin, coloring matter, and odorous principle. The chief ingredients are proportioned so that the resultant product will conform to specifications required as to appearance at the time of use, and performance in polishing floors or floor coverings.

Specification Requirements of a Floor Wax. There are a number of essential requirements that must be considered by the manufacturer of floor waxes before he can successfully market his product. The specification requirements are based upon:

(1) Odor, appearance, and color.
(2) Degree of luster obtainable after application.
(3) Wearing quality of the wax foundation.
(4) Condition of material and container after prolonged storage.
(5) Consistency of the material relative to its removal from the container.
(6) Ease of application.
(7) Drying time after application.
(8) Flexibility of polish film.
(9) Freedom from water-spotting.
(10) Washability with soap or mild detergent.
(11) Marproofness to light scratching.
(12) Freedom from slippage.
(13) Coverage per pound.
(14) Manufacturing cost.

Lesser[105] points out that while all of these factors cited by Warth[171] have received or are getting attention, particular interest has been focused on the factor of safety, as indicated by slippage. Methods and equipment for measuring slipperiness have been developed by workers at the National Bureau of Standards and in other laboratories. These provide information on the relative slipperiness of various flooring materials, floor finishes, and floor polishes. They also provide a means for evaluating the several materials that have been suggested for inclusion in floor polishes to minimize slips and falls (see Performance Tests for Polishes, p. 724).

Shellac and other resins, both natural and synthetic, are extensively used to impart slip-resistance and other desirable properties to floor polishes. Lesser[105] refers to a special colloidal silica preparation said to give high skid resistance and to impart increased gloss and decreased tackiness to floor waxes.* Although carnauba remains the most important wax in floor polish formulations, especially products of the emulsion type, Moore[118] notes that synthetic resins and oxidized microcrystalline waxes have to a large measure replaced shellac and carnauba wax in some of the cheaper brands of water-base, no-buffing, wax type floor polishes.

Gloss of Floor Polishes. The luster of the applied wax film in most of the floor polishes is directly associated with *carnauba wax*, and its extenders of natural origin, namely *candelilla, ouricury, sugarcane, esparto*, etc., and in some instances a synthetic wax, or a resin. Since the polish must spread and level out to a film which will meet the specification requirements other than luster, semihard waxes of the desired physical characteristics are used in conjunction with carnauba wax or its replacements. The semihard waxes include *beeswax, fully refined paraffin, montan, hard ceresin, oxidized microcrystalline wax*, and various synthetic waxes. The semihard waxes lend plasticity to the wax film and tend to reduce slippage, and lower costs.

Lesser divides wax floor polishes into three main classes: (1) bleached waxes dissolved or dispersed in volatile organic solvents, and provided as (a) pastes, or (b) liquids; (2) solvent-type liquid floor waxes made with a small amount of resin; (3) water emulsion floor waxes.

There are circumstances where a high gloss, or luster, is not desirable, and polishes should not be evaluated on the basis of high gloss to the exclusion of so many other desirable characteristics. The gloss should be simply classed as acceptable or unacceptable[105a].

The emulsion, or water-type liquid waxes, also called "self-polishing," enjoy the largest sales volume in the floor wax field. They are extensively used for polishing asphalt tile floors. Although formulations of this type do not necessarily have a basic odor, they are often given a scent of new-

* E.g., "Sure Step Wax" of T. F. Washburn Company, Chicago, Illinois, contains colloidal silica.

mown hay, cedar, pine, or lavender. The odorant is added to the extent of $\frac{1}{40}$, $\frac{1}{20}$, and $\frac{1}{10}$ of 1 per cent.

Floor Wax of Paste Type. Solid floor waxes are made up of carnauba wax, or its equivalent, together with softer waxes like paraffin or ceresin, and a semihard wax such as bleached montan wax, the waxes being combined with a suitable solvent, often mineral spirits and turpentine. The principle involved is that the carnauba wax furnishes luster and hardness, and that the softer waxes give the paste its consistency and solvent retention. In general the solid floor waxes in paste form comprise 30 per cent of solid waxes and 70 per cent of solvent, e.g., white mineral spirits mixed with turpentine. Mineral spirits is the name given to a refined petroleum distillate that has a boiling point range fairly close to that of balsam spirits or turpentine.

The content of carnauba wax in a floor wax is not as high as that in an automobile polish, and in general does not exceed 12 per cent. It may be as low as 3 per cent with the use of one or more good substitutes. An automobile polish requires a high wax content (18 per cent) because it is used for polishing metal surfaces. Since floors of wood absorb paraffin too freely it is necessary to keep the paraffin wax content down to 12 per cent or less. For example, a recipe for a floor wax may well read: *carnauba wax* 12; *montan wax, bleached,* 5; *ceresin wax, hard,* 3; *paraffin wax* 11; mineral spirits 60, and turpentine 9 parts. Another recipe for a floor wax calls for *carnauba wax, montan wax, yellow beeswax, ceresin wax,* and mineral spirits with a little turpentine and pine oil added, no paraffin wax being used.

The appearance of a solid floor wax in its container should be that of a paste with a smooth and glossy surface, and of uniform consistency. Beeswax and high melting point hydrocarbon waxes improve the smoothness. "Gersthofen Wax OP" is effective in the same respect. Rapid cooling after filling aids the appearance of the paste. The odor of floor wax is regulated by the addition of alpha terpineol, or any perfume which will give the wax a clean, pleasing, sanitary odor. The generally preferred colors in floor waxes are yellow and orange. Only oil-soluble colors are used.

Waxes that gel well to begin with may later produce fissures in the paste due to poor solvent retention, and this must be kept in mind when formulating floor waxes of the paste type. Ease of application and spreading is brought about by using waxes free from stickiness and containing a solvent which will not evaporate too rapidly, although the softer waxes also inhibit rapid drying, paraffin wax notably so.

The incorporation of *barium, calcium,* or *magnesium stearate* in the wax foundation of floor waxes has in times past been resorted to, since they assist in preventing undue marring and slippage, and make the polish film resistant to water spotting and to repeated washings by soapy water and mild

detergents. On the other hand these alkaline earth metallic soaps have very poor solvent retention characteristics and from that standpoint are undesirable ingredients of paste waxes. Aluminum, zinc, and other metallic soaps are also sometimes used.

Solvent Uptake of Waxes. The "solvent uptake," also referred to in the trade as the "oil uptake," and the solvent retention are two of the most important properties, aside from luster, to consider when compounding waxes for the paste and nonaqueous liquid types of floor waxes.

Of the natural waxes *carnauba* is outstanding in its solvent uptake, which is exceedingly high to produce a paste of standard consistency. In solvent retention *carnauba wax* rates high for the natural hard waxes, although not as high as *candelilla*. The hydrocarbon waxes are the best solvent retainers, but generally speaking provide very little luster. Synthetic waxes, as a whole, rate poorly in solvent retention, although a few of them do provide an excellent solvent uptake, notably "*Gersthofen Wax OP.*" The binding power consistency of the gel, and the texture, can best be rated after the wax paste is a week or ten days old. In preparing a polish paste the object is to get as many good properties, aside from luster, as possible from a combination of several kinds of wax. These good properties include binding power, consistency of gel, texture, and shelf-life.

The binding power (cohesive power) of the gels made with the hard natural waxes, such as carnauba, candelilla, ouricury, esparto, and sugarcane, is very good. It is also good with the hard microcrystalline waxes, particularly those melting at 190°F or above. Softer hydrocarbon waxes such as "Aristowax" display poor binding power.

Lux[110] has reported on the oil uptake of waxes in a numerical manner. A solution of 22 parts of pure refined ozocerite (m. 75°C) and 78 parts of turpentine was used as a standard comparate for determining the amount of solvent necessary to produce a paste of similar consistency from various waxes. By computation 354 parts of solvent per 100 parts of the ozocerite are required to give a suitable consistency by which other waxes may be compared. Penetration at 20°C of a flat-surfaced sinker was used for measuring the consistency.

The number of parts solvent per 100 parts of wax that will give the same consistencies are:

Ozokerite (m. 75°C)	354
Petrolatum wax (m. 65°C)	233
Paraffin wax (m. 52/54°C)	426
Carnauba wax, crude	900
Montan wax, crude	525
"Kara Wax"	614
"I. G. Wax OP"	1600–1900

TABLE 87. BINDING POWER AND CONSISTENCY OF GEL FOR WAXES WITH TURPENTINE

One Part of Wax to 2 Parts of Turpentine (1 g to 2 ml)

Kind of Wax	Binding Power	Consistency of Gel	Texture
Beeswax	Fair	Soft ("Vaseline"-like)	Smooth
Candelilla	Good	Medium soft	Fairly smooth
Carnauba	Excellent	Very firm	Grainy (dull mat surface)
Esparto	Excellent	Very firm	Grainy
"I. G. Wax OP"	Excellent	Very coherent and firm	Smooth and mirror surface
Japan	Poor	Very soft	Smooth
Montan, bleached	Excellent	Firm	Smooth
Myrtle wax	Very poor	Soft	Grainy
Opalwax	Fair	Soft	Grainy
Ouricury	Very good	Firm but bleeds under pressure	Somewhat grainy
Ozocerite	Very good	Fairly firm	Smooth
Paraffin	Poor	Very soft	Smooth
Peanut oil, hydrogenated	Poor	Very soft	Grainy
Petroleum ceresin	Poor	Soft ("Vaseline"-like)	Smooth
Rezo wax	Very good	Firm	Very grainy
Spermaceti	Poor	Liquid	Liquid
Sugarcane wax, refined	Good	Quite firm	Grainy
Utahwax crude	Poor	Soft	Lumpy
Vegetable wax, synthetic	Excellent	Very firm	Grainy (ring surface)
Calcium stearate	Fair	Shrink	Firm

TABLE 88. BINDING POWER AND CONSISTENCY OF GEL FOR WAXES WITH TURPENTINE-"VARNOLENE" 50:50) MIXTURE*

One Part of Wax to 2 Parts of Solvent (1 g to 2 ml)

Kind of Wax	Binding Power	Consistency of Gel	Texture
"Aristowax"†	V. good	Soft	Soft
Candelilla	Good	Some shrinkage	Fairly smooth
Carnauba	Good	Cracks	Powdery
Calcium stearate	Fair	Shrinks	Small hard cake
Carbowax	Fair	Soft, shrinks at edge	Grainy
Laurone	V. good	Coherent	Mushy
Palmitone	V. good	Coherent	Soft
Stearone	Good	Fairly firm	Somewhat powdery
Paraffin, 132/134°F (AMP)	Good	Soft	Smooth
Montan, bleached	Excellent	V. coherent and soft	Smooth
Paraffin, contact	Good	Soft	Smooth

* Examination made after 10 days of exposure of gel to ordinary room temperature.

† "Aristowax" displays poor binding power in straight turpentine and gives an oily gel.

Outstanding in paste-forming properties is "Gersthofen Wax OP." Good paste-forming waxes include carnauba, esparto, montan, and sugarcane wax. In general the hydrocarbon waxes rank below 500 in the Lux number and have poor paste-forming characteristics.

Retention of Solvents by Waxes. Waxes may be classified in three categories relative to solvent retention, when made up in a paste form with a particular solvent. In the course of several days the wax may (a) accelerate the evaporation of solvent, sometimes to a pronounced extent; (b) cause little or no change in the normal evaporation of the solvent; or (c) have a tendency to decrease, often markedly so, the rapidity of the evaporation of solvent, usually a highly desirable property.

The relative evaporative rates of solvents over a period of 48 hours or less is of the following order when gum spirits of turpentine with a loss of 27.6 per cent in weight in 48 hours is taken as a comparate:

	18 Hours *per cent*	48 Hours *per cent*
Turpentine, only	6.4	27.6
Mineral spirits (Sun Oil Co.)	4.8	13.5
Kerosene, water white	2.0	5.4
Kerosene—mineral spirits (50:50)	3.6	9.7
Turpentine—"Varnolene" (50:50)	5.8	17.9

Examples of waxes accelerating the evaporation of solvent beyond the normal amount are synthetic waxes and ouricury wax. Waxes which show a slight tendency to check the evaporation of solvent (turpentine-mineral spirits) are beeswax and carnauba. Of the hard waxes, candelilla, shellac, esparto, and douglasfir have a pronounced tendency to aid in the retention of solvent. The paraffins, stearic acid, japanwax, spermaceti, and bleached montan wax are excellent solvent retainers. "Aristowax" is perhaps the best hydrocarbon wax for retaining solvent, since it reduces solvent evaporation by 65 to 70 per cent. Of the ketones (C_{12}–C_{18}), laurone is the best solvent retainer, since it compares favorably with "Aristowax."

Ivanovszky[92a] relates that waxes decrease the rate of evaporation of solvents very markedly; this property is called "retention" (R). The "retention number" (R_z) is determined by the loss in weight in 100 grams of a 25 per cent wax in a benzene solution made under identical conditions and exposed to the atmosphere at 15°C in cylindrical dishes with a cross-section area of 133 sq mm. The retention becomes $R = 100/R_z$. For the retention of pure dilute wax solution, the relation $R_z = f_1/C_1V_1$ holds until saturation, where C_1 is the concentration and V_1 the specific retention of the dissolved wax. The retention of saturated solutions is expressed by $R_z = R_s$ maximum. Ivanovszky states that a large series of determinations show that the R of specific waxes is constant within narrow limits and characteristic numerically. R_z decreases in the following order for the waxes: crude montan, japanwax, carnauba, beeswax, refined ozocerite, microcrystalline, hard paraffin, normal paraffin bleached montan, ozocerite-ceresin mixture, soft paraffin, refined ozocerite-paraffin, and bees-

TABLE 89. WAX GELS PREPARED WITH TURPENTINE

Type of Wax	Loss In: 24 Hours (%)	48 Hours (%)	72 Hours (%)	7 Days (%)
Carnauba	5.5	9.2	16.5	34.9
Douglasfir	0.02	1.5	1.9	3.5
Ouricury	6.0	11.0	20.0	41.5
Candelilla	2.9	5.7	8.6	12.9
Esparto	3.6	7.3	11.0	23.4
"Gersthofen Wax OP"	7.0	11.1	14.7	28.6
Petroleum ceresin	3.6	7.3	9.0	18.0
Beeswax, white	6.7	13.1	16.3	37.2
Paraffin, soft	1.3	3.9	10.5	15.7
Japan	5.5	12.6	20.0	32.5
Calcium stearate	7.3	14.7	23.5	45.2
Stearic acid (triple pressed)	0.9	1.8	3.6	9.0

NOTE: Carnauba wax gel cracked at edge, "Gersthofen Wax OP" gel developed fissures, paraffin wax remained very soft, japanwax gel cracked, and calcium stearate gel showed much shrinkage.

wax-paraffin. The R_s values depend only upon the chemical properties and purity of the wax and are not related to the melting point. The addition of any wax decreases the R_s value of beeswax. A minimum R_s is given by a mixture of 97.5 paraffin and 2.5 parts ozocerite.

Where ligroine is used as a solvent, the "retention number" may be conveniently determined by employing 133.3 grams of paste made from 25 per cent of wax and 75 per cent of ligroine. A metal evaporation dish of 120 mm diameter and 25 mm height is used, and the solvent allowed to naturally evaporate at 15°C. The "retention effect" is defined by the maximum retention number obtained after 10 days and the corresponding maximum wax content.

Turpentine-Mineral Spirits Mixtures as Solvents. Pastes of waxes made with solvents in which turpentine has been proportioned with mineral

TABLE 90. WAX GELS PREPARED WITH STODDARD SOLVENT AND TURPENTINE (85:15)

(10 g wax, 20 ml solvent, exposure area 12½ sq cm)

Type of Wax	Loss In: 24 Hours (%)	48 Hours (%)	72 Hours (%)	5 Days (%)	7 Days (%)
Carnauba	4.3	10.2	8.6	14.4	17.2
Ouricury	0.6	2.8	11.4	14.6	23.0
Candelilla	4.8	9.6	19.2	28.9	38.4
Beeswax, yellow	6.8	14.0	25.2	41.7	52.2
"Aristowax"	1.3	1.4	1.5	2.8	5.7
Stearic acid*	1.3	1.6	1.8	4.3	7.0
Calcium stearate	10.1	21.6	13.3	28.9	62.3
Opalwax	6.0	14.9	29.9	68.8	86.7
Microcrystalline†	2.8	8.6	27.3	37.6	49.0

* "Hystrene S-97."

† "Bareco ES-116," 190°F/m.p.

spirits in a 50:50 or other ratio have been extensively studied. For example, 4 ml of the mixed solvent with 2 g of wax has been used. With a 1¾ square inch surface evaporation are and 96 hours' exposure to the atmosphere the solvent (½ turpentine, ½ mineral spirits) lost 29.9 per cent of its weight. The same solvent with paraffin wax 134/136°F (AMP), and 4 ml solvent for 2 g of wax, lost 26.1 per cent. With candelilla wax the loss

TABLE 91. WAX GELS PREPARED WITH SOLVENT OF TURPENTINE AND NEUTRAL SPIRITS OF NAPHTHA 50:50

Type of Wax	Per Cent Loss in Weight				
	24 Hours	48 Hours	72 Hours	5 Days	7 Days
Solvent (no wax)	10.2	18.4	25.5	41.5	56.3
"A-C Polyethylene #6"	8.4	16.2	22.2	36.9	50.2
"Aristowax"	3.3	5.8	8.2	12.5	17.0
"#13 Armowax"	8.9	17.1	23.7	40.3	56.2
Beeswax, white	11.5	19.7	28.4	38.7	47.3
Beeswax, yellow	5.0	9.6	16.0	34.8	43.6
Candelilla	4.5	9.1	13.4	23.9	33.7
Calcium stearate	18.1	28.8	38.8	60.4	74.3
Carnauba	8.6	12.6	18.7	30.0	40.1
Ceresin, artificial	11.9	19.5	23.9	33.8	40.3
Douglasfir	0.1	0.6	0.7	0.8	1.0
Esparto	9.8	14.5	18.8	25.7	33.9
"Gersthofen Wax OP"	11.1	17.5	23.4	35.5	46.0
Japanwax	7.0	8.5	10.0	13.3	16.7
Lanolin, anhydrous	7.7	13.4	19.1	42.9	58.5
Laurone	6.1	8.9	10.5	14.0	16.4
Palmitone	8.5	13.5	16.6	23.6	30.3
Stearone	10.7	19.5	26.7	42.3	56.2
Microcrystalline, white 160°F (AMP)	12.0	19.1	24.6	33.3	41.0
Montan, bleached	6.1	10.8	14.3	22.0	28.4
Myristic acid	8.3	16.3	21.7	33.8	49.8
Palmitic acid	8.9	17.6	23.9	37.1	52.0
Stearic acid	4.6	6.7	7.7	9.7	11.3
"Opalwax 10"	18.2	44.[illegible]	51.5	64.2	72.3
Ouricury	9.4	20.6	29.5	43.0	54.9
Oxidized microcrystalline M.K. 145/150 (AMP)	6.0	10.3	13.5	19.2	25.1
Paraffin, 122/124°F (AMP)	1.5	2.5	6.7	14.3	21.0
Paraffin, 133/135°F (AMP)	2.8	7.7	11.0	19.8	27.3
Paraffin, contact	10.5	18.0	23.8	36.0	46.8
Paraffin—ceresin, v. hard 190/195°F (AMP)	17.2	26.5	35.4	67.3	72.8
Black wax	3.0	3.9	5.4	8.2	11.5
Ricebran	4.8	9.8	18.1	34.0	41.5
Shellac	10.1	15.8	19.6	27.0	34.6
Spermaceti	7.6	10.8	11.8	13.5	18.0
Sugarcane	7.3	13.6	19.9	34.0	47.0

was 18.6 per cent, bleached montan 18.2 per cent, and laurone only 12.3 per cent. Sugarcane wax and carnauba wax showed losses of 26.8 and 24.0 per cent respectively. The efficacy of ketones, in the C_{16}–C_{12} range, of solvent retention is unique and remarkable. They also have excellent polishing value when used in conjunction with the harder waxes.

A comparative test made with waxes dissolved in turpentine shows a noticeable difference in solvent retention. For the purpose 2 g of the specimen wax is melted and dissolved in 4 ml of turpentine, and the mixture cooled to 20°C, and then warmed to 25°C, at which temperature it is maintained. The small glass beakers holding the wax mixtures are left uncovered and weighed periodically. Measurements of loss of solvent are accurate to 0.5 per cent, provided that the relative humidity in the room does not vary to a considerable extent.

Similar tests made on pastes prepared by dispersing 10 g of wax in 20 ml solvent which consisted of 85 parts of Stoddard solvent (high-boiling naphtha) and 15 parts of turpentine (pure gum spirits) by volume, are given below.

Since the degree of evaporation of a solvent will markedly vary with not only changes in temperature but with the relative humidity (RH) of the atmosphere to which it is exposed, it becomes necessary when determining the solvent retention power (RP) of waxes to run a blank (or comparate) of the solvent itself. Per cent RP can be determined as $\frac{a-b}{a} \times 100$, where a is the loss of weight of solvent without wax, and b is the loss with wax, over a given period such as 5 days.

Solvent retention of waxes can also be expressed graphically by plotting the "per cent total solvent lost" as abcissa against "days time exposed" as

TABLE 92. SOLVENT RETENTION POWER OF WAXES

Wax	Per Cent RP (positive)
Douglasfir	85 to 100
Slack wax, stearic acid	70 to 85
"Aristowax"; japanwax; laurone; paraffin, soft; spermaceti	60 to 70
Oxidized microcrystalline wax	50 to 60
Candelilla; esparto; montan, bleached; palmitone; paraffin, hard	40 to 50
Esparto, shellac wax	30 to 40
Carnauba	20 to 30
Beeswax, yellow; ceresin, artificial; "I.G. Wax OP"; microcrystalline, hard; palmitic acid; polyethylene wax; sugarcane wax	10 to 20
"Armowax #6;" beeswax, white	0 to 10
	Per Cent RP (negative)
Lanolin, anhydrous; ouricury; stearone	0 to −10
Calcium stearate	−40 to −50
"Opalwax #10"; paraffin—ceresin (190/195°F)	−50 to −60

TABLE 93. SOLVENT RETENTION OF BLENDS OF 195°F (AMP) MICROCRYSTALLINE WAX ("CROWN 700") AND 128°F (AMP) WHITE PARAFFIN

Per Cent Microcrystalline Wax	Per Cent Paraffin Wax	Days Time Exposed		
		2	4	6
		Per Cent Solvent Evaporated		
30	70	4	9	14
50	50	7	14	22
70	39	20	32	44
90	10	38	54	—

ordinate. The slopes obtained are more or less parabolic. Following are approximate results obtained from a microcrystalline wax ("Crown Wax 700" of Petrolite Corporation) having a melting point of 194.8°F and a penetration value of 3 (ASTM D 5-251). The mixtures contained 1 g of wax to 2 ml of solvent.

Days Time Exposed	Percentage Total Solvent Lost	
	V.P. & M. Naphtha	Turpentine
1	24	14
2	52	24
4	68	41
6	76	49
8	80	65

The differences between the solvent retention of a high-melting and hard petroleum wax and that of a lower-melting and comparatively soft petroleum wax are illustrated by Table 93. Turpentine was used as a solvent.

Use of "Gersthofen Wax Series O" in Paste Waxes. The use of "Gersthofen Wax OP," "O," and "OM" in a solid floor wax and in shoe polish imparts a number of desirable qualities. These waxes not only harden the paraffin wax constituent but produce excellent gels with the solvent, even when used in small proportions. They gel with turpentine and mineral spirits to a remarkable mirror-like surface, and impart this characteristic to the paste compound. They have excellent oil absorption capacity. Paraffin wax, on the other hand, has a relatively poor absorption capacity. Hence the combination of much paraffine with a small proportion of the "Gersthoften Waxes OP," "O," and "OM" will show a good grain to the gel and retain the solvent well. The combination permits a reduction in the proportion of carnauba wax in a given recipe, and an increase in the paraffine content, making it possible to lower cost without reducing quality.

An example of a recipe for floor wax which specifies "Wax OP" is of the following order: *carnauba wax* 8, *ceresin* 15, *bleached montan* 2, *paraffin* 24, *beeswax* 4, *japanwax* 4, *"Wax OP"* 1, turpentine 50, and white mineral spirits 90 parts. It will be noted that in this recipe the nonvolatile content is 29 per cent, and the carnauba wax content only 4 per

cent. For waxing linoleum floors a little higher wax content (4–10 per cent) of carnauba wax is desirable. The value of beeswax and of japanwax in the above recipe is open to question.

In melting the waxes for the manufacture of floor polishes overheating must be carefully avoided to prevent disturbance of the grain structure. The white mineral spirit is very slowly added in a thin stream with constant stirring while the wax melt is kept at a temperature of 90°C. The heating must be shut off before adding the solvent. The solvent may have small quantities of dipentene or dehydrin added to it, which give the solvent a balsamic odor. The pouring of the floor wax in the large tins is done at a temperature of 40 to 45°C (104–113°F). The large flat tins are first partially filled and the polish is cooled; then the tins are filled to the brim so as to avoid a depressed surface. When filling smaller tins, double filling may be avoided by pouring the polishing wax at the lowest possible temperature. The pouring vessel used should be insulated so as to hold the water at a constant temperature.

Wax Floor Powders. Wax floor powders are made particularly for waxing dance floors. They can be produced by finely pulverizing a mixture of damar resin with wax in about equivalent proportions. The wax may be a soft wax such as *paraffin*, and a hard polishing wax as *carnauba*. Batavia Damar, Pale East Indian Resin, or Batu Bold (scraped) are the resins used, as they are compatible with carnauba, paraffin, or other selected waxes. The wax is first melted and then the resin added; the combining temperature is 130 to 140°C when using Batavia Damar but somewhat higher for the Batu Bold.

The stearates, such as *calcium stearate* and *zinc stearate*, have been incorporated in dance floor powders. *Aluminum stearate* is now being used to improve the body and smoothness of the floor and to prevent slippage. In some formulations talcum or colloidal silica is incorporated in the molten wax. With talcum, the wax is more easily powdered, the floor coverage per pound is increased, and the waxed surface is better preserved under wear.

Liquid Floor Waxes. Liquid floor waxes have the same foundation base as the solid floor waxes, but very much more solvent, so that the wax or nonvolatile content may amount to only 8 to 15 per cent in the polish. It is also customary to use less volatile spirits for the solvent. The Esso Standard Oil Company markets suitable solvents for such a purpose, namely "Panoline" and "Mineral Seal Oil," which can be used with a lesser amount of mineral spirits or varnolene. A paste floor wax can be converted into a liquid wax by the addition of such prepared solvents.

Artificial waxes such as *"Rezo Wax B"* have been used effectively with paraffin waxes as a means of producing a gel dispersion with a nonvolatile content of 34 per cent in the finished product. The use of stearates in pol-

ishes has come into vogue, particularly *calcium stearate*, *barium stearate*, and *zinc stearate*. In pastes the stearates have the disadvantage of being shrinkable if used in any appreciable amount. Deguide[44] gives a recipe for a composition suitable for polishing floors as: *barium stearate* 55, *paraffine* 28, and a hard wax (*carnauba* or equivalent) 17 parts, colloidally dispersed in spirits of turpentine in a stable gelled condition.

Wax-Soap Type of Emulsion Polishes for Floors. So-called self-polishing waxes may be prepared from wax, soap flakes, sodium borate, shellac, and water. A simple formula would be: sodium soap 1.3, *carnauba wax* 8.75, shellac 2.45, sodium borate 1.05, and water 86.45 parts. Analyses of twelve brands of water-emulsion wax polishes by Glickman[68a] gave: solids 11.6 to 17.6 and *carnauba wax* 7.2 to 11.5 (average 9.84) per cent. The average composition of dry matter was sodium borate 4, wax 65, soap 17, and shellac 14. The *wax-soap ratio* was 4.01:1 and the *wax-lac ratio* 5.38:1.

Kroner devised a self-polishing emulsion wax in which the ingredients include in addition to those given above oleic acid, triethanolamine, casein, and *candelilla wax*. This emulsion polish is prepared by mixing three solutions: (a) *carnauba* (45), *candelilla* (10), *paraffin* (8), soap flakes (5), oleic acid (10), triethanolamine (5), sodium borate (3), water (414); (b) casein (15) TEA (3) sodium borate (2) water (180); (c) white shellac (10), TEA (2), sodium borate (1), water (187); to the mixed solutions is added 100 parts of water to make a total 1000 parts of polish. The total wax content of this polish is only 6.3 per cent. [Kroner, A. A., C. A., 44, 353 (1950)].

An ideal emulsion should increase its gloss after application and during the early course of wear. The water-emulsion type of floor wax is used on newer types of flooring such as rubber, where a volatile solvent wax is not suitable. Too much soap reduces the luster and the resistance of the wax film to water. The following waxes have been employed in various emulsion wax formulations: *paraffin*, *beeswax*, *carnauba*, *sugarcane*, *candelilla*, *japan*, and *shellac wax*. Fully refined paraffins of relatively low melting point, such as 124/126° AMP, are preferred for their emulsifying characteristics; japanwax is efficient but too expensive.

Wax-Resin Type of Emulsion Polishing Composition. Wax-emulsion polishing compositions containing *carnauba* and other hard luster-producing waxes may be considerably improved by the inclusion of certain resins, inclusive of maleic anhydride-modified glycerol-rosin esters. Hawley and his associates[82a] have patented compositions of the following type: *carnauba wax* 6.1, oleic acid 1.8, monoethanolamine 1.05, a resin complex (maleic anhydride 14.1, rosin 72.8, glycerol 13.1 per cent) 4.05, and water 87 parts. The wax and resin are melted together at 325°F and cooled to 225°F; oleic acid is added, and the mass stirred until homogeneous. It is cooled slowly to 205–210°F and the monoethanolamine is added.

About 50 per cent of the water is heated to the same temperature and is added with stirring. The temperature is held until the emulsification is complete; the emulsion is then diluted with the remaining water, at room temperature, and cooled to 90–100°F when it is ready for packaging.

Some of the wax emulsion polishes on the market contain not only luster-producing hard wax, but also a considerable proportion of *shellac*. Shellac is less expensive than carnauba wax, and is used to aid the leveling properties of the polish, give a quick luster, and increase slip-resistance. The carnauba wax may be blended with other waxes and resins. Both *sugarcane wax* and *polyethylene wax* have entered the field as adjuncts to *carnauba wax*. Polyethylene wax 90, paraffin 128/130°F (ASTM) 9, and palmitic acid 1 part is an example of a suitable base for use with resin in the preparation of wax emulsion polishes. A few of the modern high gloss producing emulsion polishes are said to contain almost as much shellac as wax. In the past the solid portion of the polish has seldom contained more than 20 per cent shellac. Shellac-containing polishes are marketed under various trade names by several of the leading manufacturers of polishes.

The American Gum Importers Association has published certain recipes for no-rub polishes in which a carnauba wax emulsion is mixed with about an equal proportion of Manila resin solution in a so-called formula P-183. The Manila resin solution is prepared from 30 pounds of Manila DBB, 19 gallons of water, and 12 pounds of ammonia water (28 per cent NH_3). The carnauba wax emulsion consists of 30 pounds of *carnauba wax*, 25 gallons of water, 5 pounds of trigamine, 3.5 pounds of oleic acid, and ¼ pound of caustic soda. In the latter recipe the wax and the oleic acid are melted together on a boiling water bath, the trigamine stirred in, and a boiling 4 per cent caustic soldium hydroxide solution slowly stirred in. A gel forms and the remainder of the water (boiling hot) is added. The finished polish is a mixture of 39 pounds of Manila resin with 34 pounds of the carnauba wax emulsion.

A Formula P-185 employs a thermally processed Congo melted down with the *carnauba wax*, and then emulsified with caustic soda, triethanolamine, and oleic acid, finally adding the required amount of water.

Natural resin-wax polishes may be made by melting paraffin and carnauba, sifting in pale East India resin, and thinning out with turpentine (Formula P-186) or with V.M. & P. naphtha (Formula P-187). East India resin may be formulated with beeswax, carnauba wax, montan wax, V.M. & P. naphtha, turpentine, and a little pine oil for a gloss polish (Formula P-188). Pale East India resin 18, *carnauba wax* 15, *paraffine* 17, turpentine 35, and V.M. & P. naphtha 35, constitute a formula, P-189. A solid floor polish (Formula P-190) is made from *petrolatum wax* 45, East India resin 45, and *paraffine* 10.

Rubless Floor Polishes. A rubless polish is usually a translucent wax

and water emulsion which gives a film of high brilliance with little or no rubbing when spread over a surface and allowed to evaporate. A rubless polish has advantages over wax and solvent rubbing polishes in the following respects: (1) it is more easily applied, (2) it does not need the application of polishing equipment, (3) it is subject to less adulteration with inferior polishing agents, (4) it eliminates the fire hazard attached to storage in warehouses or on shipboard. On the other hand rubbing polishes have the distinct advantage that the rubbing coat may be applied without scrubbing off the old wax; the need for water and soap cleaning is eliminated. Wooden oak floors may be marred and linoleum dried out as a result of repeated cleansings with alkaline powders.

A rubless polish may be used in the sprayer of a vacuum cleaner, which is generally equipped with a sprayer jar that can be filled with the liquid polish, a sprayer nozzle attached to a hose, and a valve which controls the spray of polish from the nozzle in a fine mist at a distance 4 to 5 inches from the floor surface. The film is water repellent and its resistance to wear increases for several hours after application of the polish. This type of polish is also referred to as self-polishing, washable, liquid floor wax.

A recipe for a rubless polish is the following: *carnauba wax* 13.2, oleic acid 1.5, triethanolamine 2.2, sodium borate 1.0, water 99.0, shellac 2.2, and ammonia water (28 per cent NH_3) 0.32 parts by weight. Melt the wax and oleic acid, using a hot water bath or steam jacketed kettle to heat mixture to 90°C. Add the triethanolamine slowly, stirring constantly until the solution becomes clear. Dissolve the sodium borate in a part of boiling water and add it to the wax solution. Stir the resulting clear mass for 5 minutes. Add 47 parts of boiling water slowly with constant, vigorous agitation until a smooth dispersion is obtained. Cool, and add 16 parts of water and the ammonia to the shellac and warm until solution is complete. Cool and add this to the wax dispersion. Finally, stir in the remaining 52 parts of water at room temperature.

In the following recipe, an organic amine, $O(C_2H_4)_2NH$, known as morpholine, is employed as the emulsifying agent. The latter boils at 128 and has the density of water. The first part of the formula consists of carnauba wax 11.2, oleic acid 2.4, morpholine 2.2, and water 67.0 parts by weight; the second, shellac 1.5, morpholine 0.2, water 15.5 parts by weight. Melt the wax and the oleic acid, add the morpholine, and stir until clear. Slowly add the water, previously brought to a boil, to the hot wax mixture with constant stirring, each small portion being well incorporated before further addition. The mixture becomes increasingly viscous when two-thirds of the water has been added. The mixture then begins to thin out and the remainder of the water may be added rapidly. The total period of water addition should be 30 to 40 minutes. A steam-jacketed kettle and a hand-

operated paddle, or a slow-speed, large-bladed propeller are recommended for successful production. After cooling the product while slowly stirring, the shellac solution is added. This has been made by warming together the morpholine, water, and shellac of the second part of the formula. The polish is then filtered if necessary. It is desirable to have the receptacle holding the finished polish equipped with a portable electric stirrer, so that the emulsified polish can be kept in a state of agitation at the time of filling to give a perfectly homogeneous product.

Self-lustering Floor Polish. The term "self-lustering polish" relates to a polish, not unlike rubless polishes previously described, that is applied to a surface such as wood, lineoleum, leather, etc., and which gives a lustrous and glossy finish without buffing or rubbing. In the manufacture of self-lustering polishes it is customary to prepare the emulsion, if the polish is of the nonabrasive liquid type, of hard wax of extremely small particle size, that is, a colloidal emulsion, with particles less than 5000Å colloidal dimension. The polishing wax may be *carnauba*, *ouricury*, *sugarcane wax*, or the like. Flint[60] prefers carnauba wax; Prince[135] prefers ouricury wax. The object is to form an oil-in-water emulsion wherein the oil phase comprises the hard wax admixed with paraffin.

According to Prince[135] refined ouricury wax 12½ parts, and paraffin wax (140/142°F AMP) 12½ parts, are melted together in a vessel. To the molten waxes is then added oleic acid 3 parts, and aminopropanol 2¼ parts, at about 100°C (212°F). A solution of sodium borate is prepared by dissolving ½ part of sodium borate in 15 parts of boiling water, and the boiling solution is added to and mixed with the melted wax mixture. At this point the wax mixture resembles caramel in consistency. Then 200 parts of boiling water are gradually stirred into the mixture, but after about half of the water has been added, the remainder of the water may be added cold. The resulting emulsion is stable for long periods of time.

To convert the wax emulsion described into a self-lustering polish it is necessary to add a dispersion of a suitable gum-resin to the emulsion. The addition of the gum-resin dispersion improves the "laying" qualities of the emulsion; it cause the emulsion to spread out uniformly on a surface to which it is applied. Such a dispersion, according to Prince[135], may be prepared as follows: Dissolve 12 parts of morpholine in 175 parts of water at 66 to 81°C (150–180°F) and stir 30 parts of Manila Loba C ground gum into the morpholine solution until the gum is dissolved. Strain the resulting solution. Then to every 7 parts of the ouricury emulsion add 1 part of the gum emulsion. The wearing qualities of such a polish, owing to its high paraffin content, are somewhat inferior to those of an all-carnauba wax polish for floor or linoleum, but equivalent to carnauba emulsions for all other practical purposes.

For a self-lustering polish for floor use a limited amount of *polyethylene wax* (e.g., "*A-C Polyethylene*") may be used with *carnauba wax* and *paraffin* in making up the emulsion with diethanolamine and oleic acid as the emulsifying agents, and then incorporating a solution of bleached shellac and sodium borate in water. Prince attempted to employ very high melting paraffin wax (m. 180°F) with ouricury wax, but this gives an emulsion of too large a particle size. He employed aminopropanol in preference to diethanolamine as an emulsifying agent.

Prince has[135] worked out a mathematical relationship which will give minimum particle size. It is represented by the equation

$$P = 120 - 0.2\,M$$

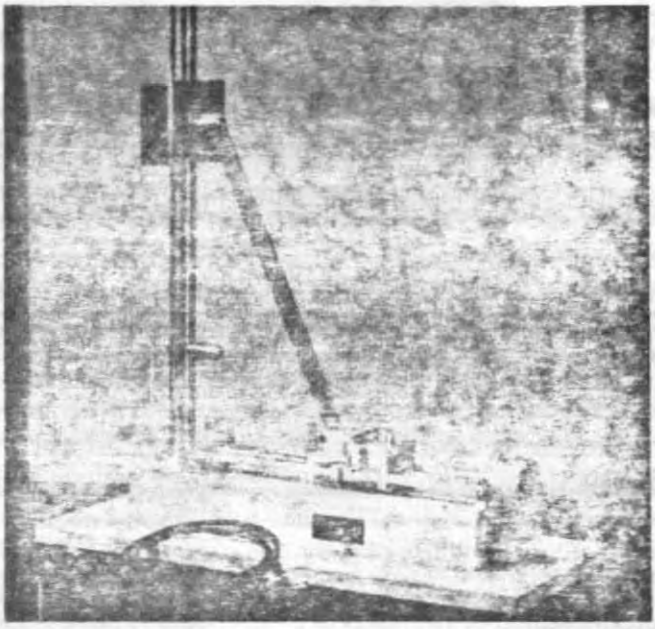
wherein M = the average molecular weight of hydrocarbon material and P = the percentage of hydrocarbon material in the ouricury-hydrocarbon mixture. Based upon this hypothesis a self-lustering polish may be prepared in which a lower melting *paraffin wax* (e.g., paraffin 131/133°F AMP) may be used with a much larger amount of *ouricury wax*, and stearic acid substituted for oleic acid.

Flint's[60] carnauba-wax rubless polish is prepared from *carnauba wax* 10, triethanolamine 1.4, oleic acid 1.4, sodium borate 1.0, refined shellac 1.4, ammonium hydroxide 0.2, and water 100 parts.

Oxidized microcrystalline waxes (OMC waxes) are easily emulsified, and are moderately hard. A polish containing only OMC waxes with phenol formaldehyde resins (e.g., "Durez 300") is reported as meeting Federal specifications for floor wax polishes. The polish is said to have good slip resistance, and to produce a good gloss.

Performance Tests for Polishes. Performance tests for polishes have not as yet been fully standardized for their evaluation, but progress is being made in that direction. *Slip resistance* is being determined by the so-called Underwriters' Laboratory and Sigler Machines; however, a standard surface is an important and unsettled factor, and there is a considerable variation in test results on a given sample. *Water resistance*, *flexibility*, *cohesion*, and *hardness* are also determining factors in standardizing polishes; also the *lustrous drying* of water emulsion waxes of the industry type. Consideration should be given to the importance of proper procedures for the cleaning, waxing, and maintenance of floor surfaces, including linoleum, asphalt tile, rubber tile, and wood.

In 1939 Fuld[65] determined the slippage of floor wax by means of a testing machine which operated on the oblique-thrust principle, and stated that the coefficient of friction for various floor waxes varies from 0.1623 to 0.3000, and that the maximum slippiness of a wax occurs three days after application.



Courtesy Dura Commodities Corp., New York

FIGURE 32. "Dura" slip-angle tester (West Germany) for determining the slip resistance of floor waxes. It operates on the oblique-thrust principle, imitating a slip forward of the human foot on a waxed surface. The degrees of slip-angle are read on a graduated scale, and may be calculated to the slip-coefficient obtainable with the Underwriters' machine.

In the new Dura slip-resistance testing machine, the foot slips forward on the floor when the angle between leg and floor is reduced to a pre-determined value, the "slip-angle"; the change of angle is facilitated by a small variable speed motor, rather than by conventional hand cranking. As the leg (e.g., leather soled) moves forward on the sleigh holding the floor surface (e.g., waxed linoleum), the angle between the arm (hinged to a weight that slides down a vertical shaft) and the horizontal plane diminishes and can be measured, aided by an actuating device, and read on a graduated scale at the base of the machine, in terms of degrees. The degrees of slip-angle, equivalent to a coefficient of antislip, can be interpreted, if desired, in terms of coefficient of friction units, by reference to a graph.

Anti-slip Agents in Floor Waxes. Various anti-slip agents are used in floor waxes. For example, colloidal silica gives floor wax a unique snubbing action. This anti-slip agent also imparts extra hardness to the floor wax. An anti-slip agent which will retain or produce a high gloss, increase water resistance, and withstand repeated damp moppings, and which is removable

with any regular floor cleaner, is preferred in water emulsion wax formulations. *Carnauba wax* can also be modified chemically to produce what is known as "hydraoxated carnauba floor dressing," in which instance the modified carnauba replaces colloidal silica for the anti-slip floor treatment. A colloidal silica agent known as "Ludox" is marketed by the E.I. du Pont de Nemours & Company, Inc., Wilmington, Delaware. A resinous material known as "Rudox" manufactured by the du Pont company is also used in floor polish formulations.

Consumption of Waxes in Polish Industry. The estimated consumption of waxes for polishes for 1951 was 34,100,000 pounds. This includes floor, automobile, furniture, and shoe polishes. The largest consumption of any one wax item was 15,000,000 pounds of *petroleum waxes*. The second largest was 8,600,000 pounds of *carnauba wax*. The other waxes recorded are *candelilla* 2,100,000 pounds, *ouricury* 1,200,000, *sugarcane* 500,000, *special synthetic* 1,000,000, *chlorinated naphthalenes* 300,000; *hydrogenated castor oil* 500,000, *Gersthofen group* 900,000, *mineral* 2,200,000, and *unclassified* 800,000.

Waxing of Enameled Ware. A composition suitable for cleaning, polishing, and waxing enamel surfaces is described by Weihe[171b]. The composition which forms a firm cake at normal temperatures contains a wax and plasticizer such as an oil or kerosene, about 13 parts; mineral spirits 65 parts, and an abrasive adsorbent such as diatomaceous earth 22 parts.

WAX IN THE FOOD INDUSTRY

The most important use of wax in the food industry is in its application to the art of impregnating or coating paper materials for wrapping or packaging foods. This particular subject will be covered on p. 779 of this chapter.

The next important use of wax, from the standpoint of wax consumption, is in the waxing of fresh fruits and cleaned vegetables. The employment of wax as a protective coating or covering for cheese is an extensive one. Other uses are in the baking industry where waxes are used as emulsifiers, whipping agents, bread and cake improvers, bread softeners, and antistaling agents. Wax is used as an antitack agent in frostings, and in sugar for dusting doughnuts. It is extensively used for coating both smoked and unsmoked sausage. Wax is used as an antitack agent for candy, and to give luster and flavor retention to chocolate confections. It finds some use as an emulsifier and whipping agent for ice cream, and as an emulsifier for oleomargarine.

Wax Coating of Cheeses. It is customary to prepare cheese, other than pasteurized or processed cheese, in the form of blocks or cylinders of varying sizes, such as midgets, twins, daisies, cheddars, wheels, or longhorns. In

the manufacture of cheese, the curd is normally pressed in a mold, the mold having been lined with cheesecloth. After the curd has been in the mold for a sufficient length of time to set, it is removed and placed in a cooler for one or two days until a partial rind has formed on the surface. When the cheese comes out of storage in the dry room, it is dipped in wax.

An ordinary composition for coating cheese may be a blended mixture 1:1 of a fully refined petroleum wax and *white scale wax* (m. 50–55°C). The petroleum wax (m. 55–60°C) can be *paraffin wax* AMP 130/132°F or a *microwax*, melting at about 140°F. Whatever the blend the white scale wax component should not be less than 50 per cent.

In the hand-dipping method each cheese is dipped from both ends with a wax-hardening interval between. For continuous line production of midgets the waxing may be done by machine, such as J. W. Greer's wax coating machine. The cheeses are conveyed on a belt through melted wax. There are two electrically heated, thermostatically controlled, melting compartments atop the machine, which will hold four bars, 10 pounds each, of wax.

Slater[153a] has described the line operation for baby Edam loaves, 8-ounce Goudas, LeRoi wedges, etc. A large tray of precut cheeses is wheeled in from the processing area and unloaded; the cheeses are wiped free of surface moisture, then placed, in four traveling columns, on a stainless steel moving belt. They are thus conveyed into an isolated room, to travel through three tier levels of belt for 25 minutes of forced-air cooling and drying. Leaving the drying room, the cheeses are next placed two abreast on the feed-in belt of the Greer waxing machine; passage through the unit takes less than 1 minute. At discharge, the coated cheeses move from the machine onto a neoprene belt where streams of cool water help set the wax. At this point they may be removed for a second coating, or continue to packaging. The waxed cheeses are wrapped in cellophane by hand, placed back on the belt, and proceed to the end of the line for boxing and weighting[199a]. The boxes are then placed in cartons for palletizing.

Gouda (ghouda) cheese is coated through custom with a red-colored wax. After the cured cheese is at least 10 days old, it is washed with warm water containing 1 per cent of ordinary blue-lime, dried thoroughly, and dipped in the prepared paraffin wax mixture heated to a temperature within the range of 150–185°F. The Groat mixture consists of *paraffin wax* 85 to 88 *petrolatum* 5 to 10, *ceresin* 1 to 2.5, and oil-soluble carmine-red dye 2 to 3 parts. The red wax envelope may be removed with ease from the sliced portions of the covered cheese. In line packing 8-ounce Goudas only a single coating is required, whereas each baby Edam receives two layers of wax.

Cheddar cheese is generally dipped in *paraffin* and moved to the curing room (50°F) where it remains for an additional 3 to 6 weeks. It is then

returned to the dipping room, given an additional coat of wax, and placed in storage at 36°F for final aging. It has been found that Danish cheeses of the cheddar type when paraffined after several weeks of curing gained 0.4 per cent in weight. The shrinkages in weight for periods of 30, 60, and 90 days were 0.3, 1.7, and 3.2 per cent respectively; and for unparaffined cheese used as control, 2.9, 5.1, and 7.5 per cent. It has also been found that less shrinkage occurs where the *paraffin* has been admixed with a *microcrystalline wax*. Slater[153a] states that the ordinary paraffin wax and even regular manual cheese-dipping wax proves unsatisfactory for machine use; accordingly, a special blend of a number of different waxes is devised for the operation, so that the resulting thermoplastic composition combines adhering qualities with a good tear-resistant texture. By using a double dip pan in the waxing machine the cheese can be moved out of the first dip into the air for partial hardening, and then redipping, thereby avoiding a bubbly melted coating caused by air being incorporated in the coat.

Peelable Coatings for Cheese. Easily peelable coatings for cheese are made by incorporating in paraffin wax an elastomer, or preferably an elastomer-wax mixture. The elastomer-wax master batch composition may have an elastomer base of cyclized rubber, polyisobutylene, polystyrene, or polyethylene combined with *paraffin*, *ceresin*, *ozocerite*, or *microcrystalline wax*. Microcrystalline wax of amber color is preferred, although brown and white waxes are also used.

Ingle and Mink proposed a coating of cyclized rubber and wax. The cyclized rubber is a hard brittle resin prepared by reacting rubber with chlorostannic acid, or a halide of an amphoteric metal (e.g. $SnCl_4$), as described in one of their patents [U. S. Patent 2,299,951 (1942)][91]. The master batch of the composition is prepared by heating paraffin to 220°F and adding about 10 per cent of the finely divided synthetic rubber resin, whence the heating is discontinued and the mixture agitated until it begins to thicken, and is then allowed to stand from 15 to 30 minutes.[92] The rubber swells at first, and when the mixture is reheated to about 220°F a homogenous liquid mass is formed, suitable for the coating operation, unless further addition of paraffin is desired.

The principle of incorporating the elastomer resin in wax is applicable to butyl rubber, polyethylene, or to elastomer blends. In commercial practice it is best to employ a master batch of the elastomer-wax blend concentrate, and for coating the cheese to disperse the latter in several times its weight in fully refined paraffin wax. The minimum amount of elastomer-wax used to secure peelability will depend upon the nature of the cheese coated and the cost of coating. In slicing the wax is peeled off, leaving rindless natural cheese. Elastomer-wax compositions are offered under trade name designations by various wax companies.

One of the various elastomer-wax coating materials is known as "Pliowax." It is a compound prepared from paraffin and a cyclized rubber resin of the Goodyear Company. It does not crystallize at refrigerating temperature and prevents loss of moisture from cheese; it has no effect upon the taste or color, and may be stripped off more readily and replaced after part of the cheese has been used. A large tonnage of cheese has been coated with "Pliowax" and this type of coating is adaptable to other food products as well.

Temperature Control in Cheese Coating. The temperature of the wax depends upon the size of the cheese. In manual dipping a large wheel of cheese the temperature of the dip may be as high as 220°F. On the other hand, in machine coating midgets the temperature of the liquid wax is held down to a few degrees above the melting point of the wax. Machine coating requires careful control of the temperature in the wax melting pan and the temperature of the circulating wax, maintenance of flow of wax to coating pan and bottomer, and regulation of the speed of the product-conveying belt. Modern equipment provides a jacketed storage tank in the base of the machine through which thermostatically controlled warm oil is circulated; from the tank wax is continuously circulated by pumps through pipes to the coating pans.

Ennis[56] advanced the idea of first dip coating the cheese in a mixture of *paraffin* and *microcrystalline waxes*, and then giving it a second coating of paraffin, such as *scale wax* to which yellow or other desired color is added. for the prime coating a composition of micro wax (m. 160°F) 60, and paraffin wax 40 parts, may be employed; and for redipping a composition of micro wax 20–30, and paraffin 70–80 parts. The treatment of the cheese is carried out just above the melting point of the wax.

Stripcoated Cheese. One of the new developments in consumers cheese packaging is the use of a composite wax and plastic coating which can be slit open, removed, and replaced for continued product protection. The new types of flexible cheese waxes contain additives which improve their adherence to moist cheese surfaces, but the best practice is to dry the cheese properly prior to the waxing operation. Since the wax coatings soil easily and are likely to become tacky if cheese is not refrigerated, they are customarily supplemented by an overwrap of cellulose acetate, "Pliofilm," "Saran," or other suitable materials. The wrapping operation may be automatic, semiautomatic, or by hand, the latter method being necessary when dealing with consumer portions of various sizes and irregular shapes. The finished package provides good protection against mold and spoilage of the product.

In the Zuercher type of packaging the composite coatings are made up of alternate layers of cheese wax and a specially formulated type of lacquer.

The plastic coating-type packages are applied to several varieties of cheddar-type cheeses cut in wedges, half-moons, and other shapes. For the application of the wax-plastic four-layer coating the consumer portions of cheese are conveyed automatically through successive dipping operations, a brief drying period following the application of each of the two plastic layers.

In waxing, the cheese portions, impaled on stainless steel carriers with projecting prongs, are automatically lowered first into the liquid wax (160°F) in the stainless steel dip tank, then withdrawn for a brief interval and immersed in the plastic compound water-jacketed tank held at a much lower temperature (about 60°F).

Prior to the coating operation the stripped cheese is cut into consumer portions by the standard type of fine wire equipment, and the cheese portions are impaled on the metal pallets which support the product while it is lowered into the dipping tanks. The time of immersion in the heated wax is approximately 2½ seconds. There is then an elapse of 30 seconds between the wax dip and the dip in the plastic solution. After the first plastic layer has been deposited, each pallet is passed through fan-equipped drying chambers maintained at 105–110°F, to quicken the drying; the drying takes about 1½ minutes. The last two coating dips—one of wax and a final plastic dip which forms the exterior of the package—are applied in substantially the same manner as above described, as is also the final drying. The cheese portions are then withdrawn from the metal prongs, and wax is used to seal the opening left by the metal fingers. The final stage of packaging consists of labeling with thermoplastic labels heated face downward on a hot plate and the cheese pressed against them, causing them to adhere tightly to the vinyl outer coating. The net weight is marked on each label[90c].

Antimicrobial Wax Coverings for Cheeses. Ingle[90] invented a means of inhibiting the growth of mold on cheese, by incorporating in the wax coating material a suitable amount of propionic acid through the agency of the addition of a smaller amount of a higher fatty acid, (C_8–C_{18}). A typical example of a wax which is effective in coating cheese wrappers (for processed cheese in particular) contains 0.3 per cent *stearic acid*, 3 per cent propionic acid, and the balance *paraffin* or other wax composition. The coating should be applied to the surface of the wrapper which comes in contact with the cheese, but may be applied to both surfaces.

The lower ethylenic acids are in general antimicrobial agents that may be added to wax coatings as, for example, the C_6 acid ($CH_3CH{:}CHCH{:}CHCO_2H$) known as *sorbic acid*, and the C_3 acid known as *dehydroacetic acid*. The latter has been marketed by the Dow Chemical Company under the trade name "DHA." The waxed paper wrapping prepared with "DHA" incorporated in the wax will retard decomposition of cream cheese by bacteria and yeasts.

A vent wrap for packaging cheese has been described by Abrams and Wagner[4]. The method of packaging comprises completely enclosing the cheese with a film of wax-elastomer composition (e.g., wax-rubber), then applying a wrap of comparatively gas-impermeable material, and sealing the seams of the outer wrapper but providing a vent whereby a portion of the gas generated during the curing of the cheese will be retained as an atmosphere about the cheeses, and the excess gas permitted to escape. This type of package is said to protect the cheese from mold growth, loss of moisture, and development of bitter flavor.

Cheese Pouches. In packaging pasteurized or processed cheese, the cheese is wrapped in a protective film or sheet, such as a wax-coated regenerated cellulose (cellophane) sheeting, preferable wax-coated MAT cellophane. The cellophane is often printed in colors, then the coating of wax applied by a pick-up roll to the unprinted side, whereupon the wax-coated cellophane is cooled and rolled up. The wax is one containing an elastomer and paraffin. A composition of paraffin and isobutylene ("Vistanex") is preferred since the cheese pouch can be more readily and safely heat-sealed in packaging. With the wax next to the cheese, a protective coating film is formed. This skin adheres to the cheese, precludes loss of water and flavor from the cheese, and prevents bacteria and molds from getting into it from outside sources; the wrapper is readily peeled from the cheese. This method of protecting fine quality packaged cheeses is proving highly successful in a commercial way.

Moist Cellophane Wraps. Batches of cheese may be treated in a somewhat different manner, namely, by coating the batch with wax of the kind above described, and then wrapping the wax-coated cheese with a protective sheet of cellophane completely moistened with an aqueous solution of glycerol and gum arabic which tends to expand the sheet and render it capable of shrinkage, and each package dried to cause the wrapper to shrink and compress the casing, as described by Fassbender[68].

Pickles with Wax Husk. Cucumber pickles, particularly dill pickles, when enrobed with a wax husk, may be stored for six months or more without danger of deterioration. After the wax coating has been peeled off by the consumer the pickle is ready to eat. The Manhattan Pickle Company, Chicago, Illinois, have marketed pickles with a peelable wax husk. The coating of the pickles with wax is accomplished by employing a belt-line coating technic in which a stainless steel meshed belt carries the product through the waxer. The liquid wax is pumped through pipes into two coating pans. In the Greer waxing machine a hand-valve allows an adjustment of wax flow to both the pans and to a flat surface at the exit of the machine, where a bottom coating is applied[152a].

A peelable wax husk has been obtained with three successive coatings of microcrystalline wax of 170°F melting point. The outside coating is a trifle

sticky. An improved husk can be obtained by two coatings of the microcrystalline wax and one thin finishing coat of paraffin of 140 to 150°F melting point to which has been added 2 per cent of polyethylene wax (mol. wt. about 2000). Pickles coated in the manner just described have a dry impervious surface.

Peelable Wax Coatings for Frozen Foods. Corn-on-the-cob has been experimentally coated for freezing by applying the same procedure as described for pickles. "Pliowax" is one of the peelable waxes suited for the purpose. The Sure-Seal Corporation, Salt Lake City, Utah, has developed a suitable wax for frozen food locker operations. Chickens, steaks, etc., may be dunked in wax to keep out moisture.

Wax Coatings for Drying Trays. Drying trays for dehydrating diced carrots, sulfited cabbage, julienne-cut potatoes, etc. may be treated with an emulsion of wax, or wax and a resin, to facilitate removal of the dehydrated product. Diced carrots are sulfited in the blancher with a one-to-one sulfite-bisulfite solution containing 0.12 per cent of total SO_2. Cabbage is similarly sulfited. The sulfiting solution tends to attack the galvanized iron trays, more so than zinc-coated screen trays. The wax emulsion is applied to the tray surface periodically by spray, brush, or dip. Some dehydrators use an oil coating if the trays have been lacquered. Waxing greatly reduces the corrosion of galvanized trays by potatoes, although in the type of emulsion used the zinc content of the dehydrated product is not entirely eliminated.

Drying trays for egg albumen are customarily made of aluminum. The treatment of such trays with an emulsion containing 14 per cent of *carnauba wax* facilitates the removal of the dried "crystals" of egg albumen, by a slight tapping of the tray.

Waxing of Baking Utensils. Baking utensils are coated with a soft oleaginous material, as prescribed by Wassermann[171a]. A composition of good stability in baking operations is formed by incorporating a small proportion of *beeswax* with almond or olive oil mixed with a hydrogenated soybean oil, or other hydrogenated oil.

Waxes as Antistaling Agents in Loaf Bread. Bread staling has been delayed, resulting in a loaf retaining good eating quality for 14 to 21 days, by adding *ozocerite* or a mixture of *paraffin* and *beeswax* to the flour. Admittedly this is contrary to good nutrition, but it can be useful for short periods under field conditions. Alcock and King[7a] noted that the most useful mixture was *paraffin* 3 and *beeswax* 3 parts melted together and blended with flour—mixed wax 28, flour 72 parts. The wax-flour mixture was used in the doughs at the rate of 4 pounds to 140 pounds of flour. Finished bread thus contained 0.4 per cent wax. Paraffin alone is less effective than the beeswax-paraffin mixture; the beeswax gives a smoother taste consis-

tency to the bread. For use under tropical conditions the addition of a mixture of acid calcium phosphate and calcium propionate acts as a rope preventative. The mixture contained flour 24, mixed wax 8, acid calcium phosphate 8, and calcium propionate 1 part. The mixture was used in doughs at the rate of 5 pounds per 140 pounds of flour.

Synthetic waxes for use as thickeners, stabilizers, whipping agents, and antistaling agents in the food industry are generally derivatives of the higher fatty acids, particularly stearic acid. In bread prepared from flour, water, yeast and salt, it has been ascertained by Pekkering and Hintzer[132] that as little as 0.5 per cent of the emulsifier improves the bread in volume, texture, softness, crumbliness, and taste. Experiments with five different types of flour showed that the emulsifier was somewhat more effective on some types of flour than others in improving the physical characteristics of the loaf. As an antistaling agent it was the most effective on a so-called "Government flour" of 85 per cent extraction and 20 per cent rye or maize. The effectiveness of the *polyoxyethylene stearate* was noticeable after the bread was a day old.

Uses of Edible Synthetic Waxes in Food. The uses of synthetic waxes in the food industry other than in the baked products is not extensive. The Glyco Products Company, New York, markets a *glyceryl monostearate* under the trade name "Aldo 33" which serves as a bread and cake improver, antitack agent for candy, as an emulsifier and whipping agent for ice cream, and as an emulsifier for oleomargarine. "*Aldo 33*" is white in color, melts and solidifies in the range of 57–61°C, and has a pH value of 7.0 to 7.8 in 5 per cent aqueous dispersion. Other esters of edible fatty acids and edible polyhydric alcohols are employed to a limited extent in the food industry. Monoesters of polyoxyethylene and glycerol combined with edible fatty acids have both hydrophilic and lycophilic properties, and therefore when used to the extent of 2 to 3 per cent (flour basis) are effective in emulsifying shortening with flour in the dough mix, and also in reducing the amount of shortening required in cake mixes.

Wax Wraps for Frozen Fish. Frozen fish is wrapped in waxed parchment paper, or in "refrigerator locker paper" (see p. 781). Large fish so wrapped is inserted in a "stockinette" of suitable size, which is then tied securely. Smaller fish, fillets, and steaks are individually wrapped in moistureproof cellophane, or coated vegetable parchment, and then placed in a proper size folding carton, which has been heavily waxed with *paraffin wax* to which a small proportion of *petrolatum wax* has been added. After closing the carton, it is advisedly overwrapped and heatsealed in moistureproof paper or cellophane. Cured meats are packed in a similar manner (see Packaging of Frozen Foods, p. 786).

Wax Coatings for Sausage. In preparing sausages, fresh comminuted

meat mixed with curing ingredients is stuffed into casings, and the individual sausages coated with wax. The coated sausages are then maintained at drying temperature until cured. Generally hot paraffin is used for waxing. The preserving of sausage has two important functions—to make it resistant to spoilage and putrefaction, and to assure the retention of the organoleptic factors such as flavor, color, texture, etc. The wax treatment imparts a better color and surface appearance to the unsmoked dry sausage. A wax coating is recommended for Polish sausage; but it must be applied only on sound, clean, well-aerated sausage in which the gas evolution after preparation has been fully completed. Wax coating is found to be the most effective means for maintaining the quality of salami for prolonged storage, and the best packing medium for shipment is finely chopped oat straw.

In the process of Kellermann[99] the sausages are coated with paraffin which has been heated to 93°C (200°F), and then applied by dipping or spraying. After the wax is set, the sausages are transferred to the standard drying room, where they are hung on racks to permit circulation of air around each sausage. The sausages remain in the drying room, which is held at ordinary room temperatures, until they are cured and dried. The former method without waxing consisted of curing the sausages in a "green room" which was warm and humid, and then after a few days transferring them to the drying room which was cool, and curing them for 2½ to 4 months. In the wax method of curing the "green room" can be dispensed with, and the curing in the dry room takes 3 to 4 months. Ennis[56] recommends dipping the sausage in a blend of *paraffin* and *microcrystalline petroleum waxes*, and then redipping in *paraffin wax*.

Wax in Doughnut Sugar. A prepared sugar for dusting doughnuts to complete their manufacture has been patented by Schlegel and Lang[145]. They specify the incorporation of about 0.4 per cent of *beeswax*, *carnauba wax*, or *sugarcane wax* with powdered sugar to obtain a food-dusting sugar. The object is to render the doughnut grease and moisture repellent, thereby maintaining a fresh appearance to the finished doughnut.

In its manufacture the sugar is placed in a steam-jacketed stirring receptacle of the kind having an inside stirrer and scraper, and supplied with steam at about 10 pounds of pressure, which raises the sugar to a corresponding temperature above the melting point of the wax, but not sufficient to melt the sugar. The wax is melted and introduced into the receptacle, which is covered, and stirred until all outward evidence of the wax has disappeared. Each individual crystal or particle becomes coated with a thin film of wax without having its appearance altered. A test for sufficiency of wax coating is to put a spoonful of the prepared sugar in a glass of water on the surface of the water; it should not sink. It can, however, be stirred into the water to give a clear solution. Incidental to the nonabsorption of

grease, a lighter dusting is required and that is an economic consideration. The taste of prepared sugar containing the wax is identical to that without wax. Thus far *beeswax* has been the preferred wax for application to or combining with the sugar.

Wax Coating for Chocolates. Care must be taken in the storage of chocolate to avoid an external condition of a high degree of humidity or too high a room temperature. If chocolate is stored in a damp place, moisture will condense on it and dissolve some of the sugar in the mixture; on later evaporation of the water, the sugar crystals will appear as a "gray bloom" on the surface of the chocolate. Proper working of the chocolate so as to keep the cocoa fat well distributed, together with good tempering, will prevent the sugar bloom, and so will the addition of a stabilizer such as lecithin to the mix. When the storage room is too warm, the cocoa butter in the mass will melt and expand, and the less dense fat will rise to the surface of the chocolate and when chilled, result is a greasy film known as "fat bloom." The fat bloom is not as apt to occur with well conched chocolate.

This difficulty in keeping chocolate, particularly the grades produced by the mechanical dippers known as *enrobers*, has led to treating of the enrobed chocolate with a very thin protective coating consisting of a thin alcoholic solution of shellac, or of benzoin, or a mixture of both. The coating can be applied by spray. *Carnauba wax* and *sugarcane wax* are being used for the same purpose where a luster is desired. Confections coated with wax keep well, do not mold, and preserve their appearance and flavor.

The effect of the addition of modifiers as "fat bloom retardants" has been investigated by Easton and his associates[61a], and particularly promising results have been obtained where approximately 1 per cent of a mixture of *sorbitan monostearate* ("Span 60") was added to chocolate. Commercial-scale trial runs have been conducted which indicate that the shelf-life of the modified chocolate is considerably increased over a similar unmodified product. The addition of 1 per cent of "Span 60"-"Tween 60" proportioned 60 to 40 to a sweet chocolate lecithin-free coating causes a slight decrease in viscosity and gives it excellent protection against bloom. Experiments with chocolate ranging in fat content from 31.7 to 36.6 per cent and in lecithin content from 0.0 to 0.22 per cent show that the addition of emulsifiers usually causes a slight viscosity increase. In these experiments by Easton and co-workers[61a] the enrober room was kept at 80°F, the packing room at 56°F, and the tunnel at 48 to 54°F with a 5 minute pass.

A cocoa-type coating for use on confectionary rations that withstand temperatures up to 49°C (120°F) for long periods of time and at the same time cannot be differentiated in palatibility from regular fine chocolate coatings has been developed by Alikonis and Farrell[7b]. The advantage of the added emulsifiers (nonionic surface-active agents) is that they keep the coating

from sticking to the wrappers and eliminate the greasy feeling associated with the use of *hydrogenated vegetable fats*. The vegetable fats melt at 99 to 120°F, but soften between 86 and 99°F. The emulsifiers not only include the monostearates, "*Span 60*," and "*Tween 60*" previously described but also the tristearates, "*Span 65*," and "*Tween 65*." A summer-type coating may be prepared from cocoa powder (10 per cent cocoa fat) 7.5, vegetable fat 32, vanillin (1 oz) 0.0625, "Span 60" 0.5, "Tween 60" 0.5, and sugar 59.4 parts. The following formula of a chocolate-type coating for molded "enriched chocolate disc" meets the rigid Quartermaster requirements: sugar 50.3; hydrogenated cocoanut oil (m. 110–114°F) 16.6; whole milk solids 16; chocolate liquor (54 per cent cocoa butter) 17.1; "Span 60" 0.5; "Tween 60" 0.5, parts. Thiamine chloride is added to the extent of 12 mg per ounce.

Dark sweet-type chocolate coatings contain not less than 17.5 per cent of cocoa powder (10–14 per cent cocoa fat) and not more than 38 per cent of sugar; whereas the light sweet-type coating contains not less than 7.5 per cent of cocoa powder and not more than 49 per cent of sugar. The nonfat milk solids 12 per cent, added fat (m. 110–114°F) 30 per cent, lecithin 0.2 per cent, "Tween 65" 0.5 per cent, salt, and flavoring material are substantially the same for the summer-type coatings. Sugar is often partially replaced by sorbitol or sorbitol and corn syrup. Chocolate is cooled between 86 and 88°F, then slightly reheated to 89–90°F before delivery to the coater.

Before the chocolate is molded, it is invariably brought to a predetermined fluidity or viscosity with *cocoa butter*. *Lecithin* reduces the viscosity of chocolate, and hence cuts down on the amount of cocoa butter needed and also the cost. Frequently the confectioner may need lecithin in the enrober when his coating for starch cast candies has thickened, and he will thin the coating by putting 1 or 2 ounces of lecthin in the enrober pot. Normally 2 to 5 ounces of lecithin is used with 100 pounds of the coating. Lecithin is an antioxidant and hence will extend the shelf-life of caramels by retarding staleness and rancidity.

Sapogenic waxes of fruit skins have been suggested for moistureproofing confections (see p. 298).

Wax Treatment of Vegetables and Fruits. The processing of fresh fruits and vegetables in their preparation for the market has, according to Sharma[150a], two general purposes. The first of these is to see that the fruit or vegetable is clean; the second is to do whatever possible to retard the withering or shrinkage of the commodity, so that it will be in as fresh a condition as possible when delivered to the ultimate consumer. Many farm products, such as carrots, rutabagas, potatoes, and the like, are more or less dirty when harvested. In order to clean these, they are put through a

washing process. Nature provides most fruits and vegetables with a natural waxy coating to protect them from drying up and withering. The washing process tends to impair this natural coating, and it has been found that the shrinkage rate for these products can be greatly reduced, after they have been washed, by the addition thereto of relatively small amounts of a preservative coating of wax. The coating of citrus fruits is, perhaps, the oldest application of such wax treatment.

There are devious ways of applying wax to fresh fruits and vegetables. Types of waxing are as follows:

1. Waxing with an emulsion of wax in water.
   a. Waxing by dipping vegetables in liquid emulsion.
   b. Waxing by running vegetables through emulsion foam.
2. Waxing with a solution of wax in an organic solvent sprayed on the vegetables.
3. Waxing with melted wax, or dry waxing.
   a. Waxing by dipping vegetables in melted wax.
   b. Waxing by atomizing melted wax in a warm chamber wherein the vegetable is waxed or the fruit is brush-polished.

The waxes used in the wax processing of fruits and vegetables are generally mixtures of one or more hard waxes, such as *carnauba*, *ouricury*, or *sugarcane wax*, with *paraffin wax*. Petrolatum or white mineral oil is sometimes used as a softener. A hard wax is necessary to impart gloss. Since large volumes of produce are wax treated, machines were developed to mechanize and accelerate treating. These are controlled by their originators and patentees who permit their use on various contractual engagements.

Manufacturers of fruit and vegetables who produce waxing materials and equipment in the United States include the Brogdex Company, Pomona, California; the Dow Chemical Company, Midland, Michigan; the Food Machinery Corporation, Lakeland, Florida; the Franklin Research Company, Philadelphia, Pennsylvania; and S. C. Johnson and Son, Racine, Wisconsin.

Greenstreet[73b] formulated a solid wax composition suitable for application to the fruit and vegetable bodies by brushes in any atmospheric temperature ranging from 32°F to at least 100°F. To each 100 pounds of paraffin wax (128/130°F-AMP) from 1 to 2 per cent of carnauba or other suitable vegetable hard wax is added and the two ingredients are heated to about 210°F to effect fusion. The mixture is cooled to 200°F and 50 to 100 fluid ounces of sulfonated mineral oil are added and thoroughly admixed with the melted waxes. The mixture is then poured into molds at approximately 190°F and allowed to cool and set or congeal into the desired solid block. In very hot climates about 2 per cent of the carnauba wax or replacement is used and only 50 fluid ounces of the oil. In cold climates the minimum of

hard wax and optimum of sulfonated oil is employed. The Greenstreet composition may be applied to wet fruit as well as dry fruit with the same desirable results, which is not true of ordinary wax slabs.

Equipment for Processing with Wax Emulsions. The use of wax emulsions has been generally recognized by growers and shippers as the most effective method of preventing desiccation and improving the appearance of fruits and vegetables. Perishables such as citrus fruits, apples, pears, melons, turnips, carrots, sweet potatoes, cucumbers, squash, potatoes, tomatoes, and eggplants are treated with wax emulsions in suitable equipment, before being packed for shipment.

The equipment generally consists of a waxing-tank, say 10 feet long and 2 feet wide, of 12-gage steel, and skidded on channel irons so that it can be easily moved by placing wooden rolls under the skids. The waxing-tank has a sloping bottom so that a minimum of waxing emulsion is required at the lower end, in which the fruit or vegetable to be treated is immersed. The tank has a conveyor belt which conveys the produce through the emulsion and into the drier. When using a tank of the size described, 100 to 120 gallons of emulsion are sufficient to give ample coverage over the lower end of the conveyor belt.

The conveyor belt is of sufficient length to permit draining the waxed product before it reaches the drier. The belt is made of steel wire and carries light wooden slats that will move any type of produce. The drier is equipped with a wooden roll conveyor belt which is designed to turn the waxed produce slowly as it passes through the drier. The drier is about 3 feet wide and 16 feet long, and is open at the bottom. It also has slides in the sides so that the air, picking up moisture from the fruits and vegetables, is allowed to pass quickly out of the drier. In the top of the drier of the Korb-Pettit Wire Fabrics and Iron Works, Philadelphia, over the conveyor belt, are located four 22-inch propellor-type fans. To insure perfect and quicker drying on humid days there are twelve 500-watt electric heating units located under each fan. The oven is equipped with an adjustable discharge plate.

Wax-and-Water Spray Emulsions. Apples, pears, and citrus fruits are waxed by means of a spray treatment with emulsions formulated from waxes and emulsifying agents and water. For coating citrus fruits, cantaloups, apricots, and tomatoes, Sharma[150] employed an emulsion of the following composition: sodium hydroxide 6, triethanolamine 20, stearic acid 42, *paraffin wax* 105, *carnauba wax* 55, shellac 100, and water 2000 parts. This composition is further diluted for use. The spraying of fruit with waxy emulsions in which an amine soap is used as an active emulsifying agent has also been advocated by Cothran[37], of Pomona, California. Providing fresh fruit with a waxy coating of this character, while it is packed for shipment from the producing sections, has now become standard prac-

tice with a large proportion of commercial fruit packers and shippers. The surface of the fruit must not be sealed so completely as to interfere with its so-called "breathing."

Formulations of Wax Emulsions. There are numerous formulations of the wax emulsions used in wax processing of fruits and vegetables; many of the formulations are patented.

Emulsions may be prepared from *paraffin wax* 5, mineral oil 2½, emulsified with stearic acid 5, triethanolamine 2½, and water 85 parts. A heavier emulsion may be prepared from *paraffin* 7½, white mineral oil 1, oleic acid 1, triethanolamine 1, and water 89½ parts. Oranges, lemons, tangerines, melons, avocados, tomatoes, limes, etc., all satisfactorily respond to the wax emulsion preservative treatment. Brushing or rubbing of the fruit to finish the protective coating is not required although sometimes it may be desirable. Benefits from waxing are greatest on fruits having a thin cuticle, with the possible exception of the apricot. Waxing reduces water loss but does not overcome decay.

Handy[73] claims to have formulated a wax emulsion which is effective and inexpensive, and gives a lustrous coating to the fruit, a coating which is free from tackiness. The emulsion is prepared by melting together *candelilla wax* 7.67, *paraffin* 1.54, and oleic acid 2.5 per cent with subsequent addition of 0.35 per cent sodium hydroxide and water at 210°F. A shellac-ammonia solution is added to make the final concentration of water 84.33, shellac 3.00, and ammonia (NH_3) 0.54 per cent.

Cold injury to grapefruit stored for five weeks at 39°F has been effectively reduced by coating the fruit with an emulsion of *paraffin wax*. The wax emulsion may be made up with *paraffin* and *carnauba wax*. A soap of triethanolamine and stearic acid is used as the emulsifying agent to disperse the waxes. The desirable amount of waxes in the emulsion is 4 to 5 per cent. A little pure-white mineral oil in the proportion of 1 part of free oil to 5 parts of the waxes is said to give a more continuous coat of wax to the fruit, and permits the use of a thinner film.

Griffith[74] recommends melting together 3 parts of a vegetable wax such as *carnauba* with one part of *paraffin*; to the homogenous molten mass is added an anhydrous organic amine soap of a higher unsaturated fatty acid (e.g., the triethanolamine soap of oleic acid), and after thorough mixing, small increments of hot water (200°F) are added into the mass while maintaining a temperature of at least 210°F, continuously stirring until the total amount of water has been added to produce an emulsion of the desired consistency.

Waxing materially reduces the percentage of wilt and loss of weight of apples given any preripening treatment. Wax emulsions applied to bananas slow the ripening to 7 to 8 days from the normal 5 to 6 days.

A wax emulsion, patented by Towner[163a] in Australia, consists of *shellac*

wax, a sodium soap or borate soap of a higher fatty acid, sulfonated *cetyl alcohol*, *paraffin* or *ceresin wax*, and shellac. It can be used for coating fruit or vegetables.

Processing with Melted Wax. For the overwinter storage of sugar beets used in planting, the mother beets when coated with *paraffin wax* and stored show no material decrease in the sucrose content; although the coating reduces transpiration it does not cause the beets to deteriorate. It is desirable to apply the paraffin coating at low temperature to prevent loss of moisture and remove it at planting time.

Haller[76] of the U. S. Department of Agriculture, Beltsville, Maryland, found that dipping turnips in hot, melted paraffin (96 per cent *paraffin wax* and 4 per cent resin) produced a relatively thick coating and greatly reduced the weight loss, reduced sprouting, and prevented new roots from forming. The paraffin coating also retarded gaseous exchange so that the CO_2 evolved and O_2 consumed were greatly reduced. No off flavors result by the processing treatment.

Processing with melted wax enhances the pleasing appearance of the vegetable or fruit, but is only applicable to produce which is to be peeled, and hence has a much restricted use. Wax is not readily removable by boiling vegetables such as turnips, carrots, beets, cabbage, and potatoes.

Spray Waxing. The dry method of spray waxing previously in general use involved the atomization of molten *paraffin* containing a little *carnauba wax* into contact with the fruit in a chamber heated to 180–220°F, wherein the fruit was briskly rubbed with horsehair brushes to spread the small quantity of molten wax deposited on the entire surface of each fruit. This treatment cut down the rate of withering by 30 to 40 per cent.

Cucumbers, sweet potatoes, rutabagas, or the like are spray waxed to retain flavor, improve appearance, and prolong the storage life. Suitable dye concentrates may be added to the wax to improve the color of the sweet potato or other vegetable. "*Micriswax*" with the addition of a few per cent of a natural or edible synthetic wax can be used as the spray material for watermelon and other vegetables.

Prepackaging of Oranges. Valencia oranges are washed with soap solution at 110°F, waxed with "Flavorseal," and packaged two days after harvest. Bags of perforated "Pliofilm" permit transpiration of fruit, permitting storage of several weeks at temperatures ranging from 38 to 78°F. Washington naval oranges are treated with ethylene for 60 hours at 55°F, washed with soap solution at 114°F, given the application of cold slab wax, and packaged four days after harvest.

Wax and Solvent Spray Method. The use of a solution of wax in a volatile solvent for spraying fruits and vegetables was advocated by Sharma[150a] in 1942. It is claimed that this method has distinct advantages: (a) the wax is

easy to apply; (b) it may be applied without damaging the fruit or vegetables in any way; (c) the solvent dries quickly, thus rapidly incorporating the applied wax with the natural protective coating of the fruit; (d) the process is economical in the use of applied wax; and (e) the method permits a shrinkage control, and regulation in the amount of wax so as to provide adequate respiration of the fruit while it is en route to the market.

The content of wax in the spray solution is fixed at 7 per cent, and a wax with minimum cloud point of 34°F is specified. For example, one may use 3 per cent *coconut fat* plus 4 per cent *paraffin*, or 3 per cent *spermaceti* plus 4 per cent *paraffin* in the spray emulsion.

Canteloups grown in the Imperial Valley, California for shipment to the East Coast have been wax processed after fumigation with a chloramine, specifically nitrogen trichloride. The waxes tried by Pentzer and his associates[132a] consisted principally of *carnauba wax* and *paraffin* in proportions of about 3:1, and differed in the type of emulsifying agent used and the concentration of the wax materials in the water emulsion. Tests were also made with a solution of wax in a volatile petroleum solvent, applied as a fine spray to the melons. This solution of wax and the water emulsions were held at temperatures of about 110°F in the equipment used for the application. It is said that by proper waxing the life of a canteloup may be extended by 15 days although this is not borne out by the experiments of Pentzer *et al.*[132a], who have concluded that there is little commercial advantage from waxing cantaloups.

Waxing of Vegetables. The coating of tomatoes with wax is being successfully accomplished by the use of wax emulsions prepared from suitable waxes, emulsifying agents, and water as described in the Sharma patent for waxing fruits. Striking redution of weight loss and spoilage is brought about by wax treatment of greenhouse cucumbers stored during three weeks in an ordinary midsummer. Mack and Janer[111a] treated the cucumbers with a water emulsion of a wax mixture of *carnauba wax* 75, and *paraffin wax* 25 parts, designated "Brytene No. 284-D" by the manufacturer, the Franklin Research Company, of Philadelphia, Pennsylvania. The emulsion, which contained 35 per cent of the wax mixture, was diluted at the rate of 1 part by volume of the emulsion to 6 of tap water, and the cucumbers were immersed until thoroughly covered, then removed and allowed to drain and dry.

Potatoes can be treated with an aqueous wax emulsion in a manner that will inhibit the growth of sprouts when stored at 70°F, and impart an attractive glossy appearance. Newhall[124a] employed an aqueous emulsion prepared by melting *candelilla wax*, *microcrystalline wax*, oleic acid, and a methyl ester of 1-naphthaleneacetic acid in a suitable vessel; to this, sodium hydroxide solution and triethanolamine are added, and sufficient water to

obtain an emulsion with 28 per cent solids. The emulsion may be applied by spraying or dipping. The processing coat is said to average about 5 cents for 100 pounds of potatoes. This so-called "Certifresh Process" is licensed by J. C. Johnson & Son, Racine, Wisconsin.

In waxing turnips at Beltsville, Maryland, Haller[76] employed a waxer in which a froth of the emulsion overflows onto revolving cloths that apply it to the turnips, which pass beneath them on a roller conveyor. Drying was then done by conveying the roots under a series of heat lamps in a drying tunnel.

Carrots, celery, and radishes are thoroughly cleaned and waxed for long-distance transportation. The waxing is accomplished with a special patented foam waxing machine, which coats the entire surface of each piece of produce with a microscopically thin, even film of wax. Oranges, bananas, cucumbers, grapefruit, bell peppers, and sweet potatoes are some of the products which are coated in this manner.

Commercial tests by the Food Machinery Corporation in cooperation with the California eggplant producers prove that the vegetable will stay fresh and marketable many days longer when protected by a thin, porous, wax film. "Flavorseal" is the brand name of one of the waxes which is applied by a special machine at the packing house to ten fruits and vegetables (Journal of Commerce, N. Y., Aug. 6, 1948). In addition to eggplant and tomatoes, the fruits treated were oranges, lemons, grapefruit, tangerines, cucumbers, bell peppers, cantaloups, and persimmons.

Nurseries have found it advantageous to spray cacti with wax emulsion when they are to be packaged for distant shipment. Florists also use wax emulsions to preserve the bloom of cut flowers, such as cut roses.

Waxes for Wax Treating. The waxes used in wax-treating fruits and vegetables are generally mixtures of one or more hard waxes with paraffin wax, for example, *carnauba* and *paraffin*, or a blend of *carnauba*, *ouricury*, and *sugarcane waxes* with the paraffin. Deresinified *candelilla wax* has also been employed with paraffin, or with *ceresin*, *ozokerite*, and *japanwax*, for water emulsion types. An all-vegetable wax, such as *canesugar wax*, can now be applied to fruit and vegetables in emulsion foam, and then polished to a bright luster by the use of cloth flaps on the automatic conveying belt.

Wax Colorings for Fruits. In preparing light-colored fresh citrus fruit for the market it is desirable to not only retard the withering or shriveling, but to produce a glossy and shiny surface of desirable color to the rind. Sharma[149] enhanced the varietal color of citrus fruits by applying to the whole fruit a waxy mixture containing particles of coloring such as a suitable oil-soluble dye. The waxy mixture in a heated, finely divided state is applied to the whole fruit, and the fruit is finally brushed at a temperature sufficient to soften the waxy mixture applied and cause the coloring substance to pass into the skin or peel of the fruit.

Cothran[38] found that improvement could be effected in the commercial grading of lemons by the application of a greenish-colored wax material to the surface of the fresh fruit. A glossy surface to the lemon is generally preferred to a dull surface, and also a so-called "true lemon-yellow" color.

In regular practice the wax coating is applied to the lemons just before the final grading and shipment, or it is applied prior to storing or curing the fruit. The lemons brought in from the groves may be thoroughly cleansed with a warm sodium borate solution, rinsed with cold water, and dried; or otherwise cleaned. A very thin coating of suitable waxy material is then applied. The wax commonly used is *paraffin*, or paraffin admixed with white mineral oil. This treatment imparts too deep a color to the lemon, so Cothran proposed a tint to the glossy transparent waxy coating within the blue-green range. Typical dyes suitable for use are various oil-soluble greens referred to in the patent specifications. These dyes constitute but a fraction of one per cent by weight of the waxy material used for the protective coating. Ordinarily 1 part of dye to 2500 or 3500 of wax may be used, and is sufficient to correct the color to a desirable shade of "lemon yellow." Cothran claims that where the molten wax material atomizes or fogs upon the lemons, as they pass over the polisher brushes, a suitable composition consists of 99 parts *paraffin*, and 1 part *carnauba wax*. With no accompanying nonvolatile oil, a higher polish is obtainable, which may be further improved by increasing the proportion of carnauba. The slightly amber tint of the carnauba can be offset by a little additional dye in the wax composition. The same principle is applicable to the emulsion spray process of treating fruits.

Waxing Berry Hallocks. In recent years it has become the custom to treat hallocks—small wooden berry boxes—with wax. The wax treatment not only enables the grower or packer to carry the hallocks over from one season to another without the concomitant danger of mold growth, but renders the waxed boxes more sanitary and easier to wash with a cold-water spray; neither water nor berry juice will penetrate the waxed wood. The wax processing also avoids the need of cleaning with steam or disinfectant.

The wax coating process used by the C. S. Kale Canning Company, Everson, Washington, is that recommended by the USDA laboratory at Albany, California. The new air-dry boxes are dipped in paraffin wax heated to 65–66°C (150°F). The object is to produce a film thick enough to serve as an adequate water barrier, but thin enough so that it will not present a sticky surface to the fruit.[85]

A wax mixture consisting of *fully refined paraffin* 95, and *microcrystalline wax* (m. 160/165°F—AMP) 5 parts, has been suggested by Barta and Lowe[11a] as being very effective. They recommend that the dipping treatment of the berry hallocks with the molten wax be conducted at a temperature of 15 to 20°F above the melting point of the wax mixture. The time

of dip is not less than 15 seconds, and it takes about 40 seconds for the wax to congeal. One hallock will pick up 0.6 ounce of wax, equivalent to 36 pounds per 1000 boxes. The total cost in 1949 was estimated at $3.80 per 1000 boxes.

The fact that waxing has made it possible to clean hallocks thoroughly with a good, stiff spray of cold water has led to the development of a Ferris wheel type washer (octagonal with eight flat surfaces) which readily cleans the boxes while still in the "flats," streamlining the operation and conserving plant space. The cleaned hallocks are then again ready for their journey back to the fields. A washer of the Kale type has a capacity of handling 1200–1500 hallocks per hour.

WAX IN THE LEATHER AND RUBBER INDUSTRIES

Waxes are extensively used in the leather industry. Wax is used in the stuffing grease employed in preparing "waxed splits." Finishing waxes are used for finishing bootsoles. Wax is used as a "resist" in the art of staining leather for the preparation of so-called "antique leathers." In the industrial application of seasoning to leather by mechanical brushing, wax is used as a base for the brushing compound. For this purpose *carnauba wax*, *ouricury wax*, or a *carnauba replacement wax* is used. Soft brush-polish finishes are prepared with the aid of *japanwax*, or so-called *japan replacement wax*, or by means of emulsifiable material having wax in its composition.

Leather preservatives often contain wax. Wax also provides the foundation of various kinds of leather polishes and dressings. *Montan wax* is used with other waxes, drying oil, and coloring agent in wax sticks employed for covering defects in leather. Wax is the polishing constituent of saddle soap so commonly used to clean, polish, and preserve leather goods. *Oxidized microcrystalline waxes* are of considerable value in the preparation of leather dressings.

Stuffing Compositions. Leather is stuffed to make it reasonably water-repellent by the application of a composition of oils, greases, and waxes. A stuffing grease for waxed splits may be prepared from tallow 45, *woolwax* (anhydrous lanolin) 10, *stearic acid* 25, and *paraffin wax* 20 parts. From 35 to 40 pounds of stuffing is used to 100 pounds of dampened splits. The drum is rotated and heated to 125°F and the grease to the same temperature. It is then run with splits and grease for 20 minutes with the door closed and 10 minutes with the door open. The splits are then hung until they are well cooled off and stiff. They are then set out lightly on the back and then on the face side and hung up to dry. The drum is customarily heated with live steam.

Either wet leather or dry leather may be stuffed. In stuffing wet leather the tanned stock must be wrung, or in stuffing dry leather it must be damp-

ened, for treatment. One-hundred pounds of dry splits will carry 110 pounds optimum of stuffing grease. Other waxes used in the stuffing art are combinations of oils, greases, and waxes such as carnauba, *microcrystalline*, and *paraffin*. The stuffing materials are combined in different ways to obtain the desired characteristics in the finished leather; for very water-repellent leather, only the waxes are used. For leathers that are subjected to much flexing a combination of oils, greases, and waxes is needed. Occasionally dry leather is stuffed by hot-dipping it in a mixture of high-melting fats and waxes, or subjecting it to a "burning in" operation in which the hot, dried leather is placed on a table and a hot molten grease mixture (195°F) is poured on the flesh side only, thereby maintaining good color on the grain.

Wax Seasoning for Leather. Seasoning materials for leather may or may not contain waxes; they may not contain waxes when the leather is to be glazed. They are usually applied to leather by hand with a swab, a thin 4 inch x 12 inch block of wood with plush having a strap across the back under which the hand is slipped. Seasoning machines are also in general use. From one to five coats of seasonings are applied, each coat being allowed to dry before the next is applied. The concentration of seasoning materials used, such as egg albumen, is ½ pound or less per gallon. If a brilliant luster is desired, the leather is glazed. Glazing is done by a 2½ inch diameter cylinder which is moved rapidly across the surface of the leather under high pressure. The heat generated by the friction causes the seasoning to take on a high luster. Seasonings containing waxes in considerable proportion are not glazed because of the frictional heat which would streak the wax. This type of wax seasoning is usually brushed to produce the luster. The brushing machine carries a revolving brush which will give a high polish to the leather drawn through the machine. *Carnauba wax* or *sugarcane wax* can be dispersed in water with casein for seasoning. For pigment finishes stock solutions are made up of one pound to the gallon.

Carnauba, or *candelilla wax*, and *beeswax*, are dispersed in soap solution for leather finishes. Waxes are used for their relative softness and tendency to maintain the "leathery feel" as well as to provide luster when the finish cannot be glazed.

According to Davidsohn[40] a soft brush-polished finish suitable for application to shoe calf is obtained from an emulsion prepared from *beeswax* 5, *carnauba wax* 1, olive oil soap 5, ammonia 1, glycerine 1, and water 100 parts. The soap is dissolved in 50 parts of hot water and the ammonia added. The waxes are melted separately and added with stirring to the soap solution maintained at about 90°C. The remainder of the water is then added to the properly prepared emulsion together with the glycerin.

Leather Preservatives. In the industry the purpose of a leather preserving oil or wax is to retain the natural grease or oil of the leather; to waterproof the leather against rain, snow, and sleet; and, if the preservative is applied to shoes or boots, to keep the feet warm. Marine oils are used as preservatives, as are also mixtures of fish-liver oil and castor oil. Neatsfoot oil is also used. *Anhydrous lanolin* (woolwax) is a good preservative for leather articles. A suitable soft product can be prepared from anhydrous lanolin 2, *scale wax* 3, and mixed fish and castor oils, 6 parts. Solutions of lanolin, up to about 30 per cent, in mixtures of benzene and turpentine are suitable preservatives for transmission belts and other leathers. Tallow and colophony have been used to modify paste compositions, as well as *ceresin wax*, *Utahwax*, and the *microcrystalline waxes*. *Polyethylene wax* may be added in small amount to increase the firmness of woolwax, in leather stuffing compositions. The *crude black montan waxes* used for leathers are being replaced by somewhat similar black microcrystalline waxes refined from petroleum.

Leather Dressings. The object of a leather dressing is to prepare and preserve the finish of leather goods. The formulation of the dressing is quite dependent upon the use to which the dressing is put, there being no all-purpose dressings. Leather dressings are conveniently classified as to their consistency. They are prepared in three forms: liquid, solid paste, and powder.

The best-known leather dressing and the one most widely used is saddle soap. There are innumerable brands of saddle soap on the market. The consistency of saddle soap is that of a solid paste, and it is usually applied to leather by means of a damp sponge or cloth in such a way as to clean the leather, after which the leather can be easily rubbed to a polish with dry flannel or other suitable material. An unpatented formula of Lidard is *beeswax* 50, *carnauba wax* 15, trisodium phosphate 5, castile soap 25, water 120, and turpentine 25 parts. Oil-soluble yellow is added in minute amount. In preparing the dressing the waxes are first melted and the trisodium phosphate, in half of the water, is added very gradually to the melted waxes at a temperature of about 190°F and with considerable stirring to permit the waxes to emulsify. Then the castile soap dissolved in the other half of the water is added with stirring. Finally the turpentine is added and the whole poured hot into the jars.

A leather dressing prepared by Sajak[143] for miscellaneous uses consists of a mixture of waxes, such as *beeswax* and *spermaceti*, in sperm oil and castor oil. The product is of the consistency of a paste. A product known as Stack's belt-dressing is prepared from rosin 61, *beeswax* 8, linseed oil 7, heavy grease 7, pumice stone 16, and oil-soluble color 1, parts.

For dressing finished suede and chamois leather after cleaning, a prepara-

tion of liquid petrolatum, or white mineral oil, diluted with suitable solvents, inclusive of high-boiling naphtha, can be used. French polishing powder for leather may be prepared by melting together *carnauba wax* 60, colophony 30, and *paraffin wax* 10 parts. When the melt has become chilled it is finely pulverized, and packaged for use.

Razor strop dressing can be made by intimately intermixing an abrasive powder and a mineral lubricant powder with melted waxes and then molding the resultant product in stick form. Kazda[98] prepared a razor strop dressing from pulverized carborundum 5, *paraffin wax* 75, *beeswax* 10, and graphite 10 parts.

Leather Polishes. In the preparation of a paste polish for application to leather goods, it is desirable to use a wax of high-turpentine adsorption value, and which at the same time produces a high gloss by rubbing after the polish has been applied. An example is the polish proposed by Langenhagen[102] of Leipzig, Saxony, which is prepared from *carnauba wax* 40, stearate 1, oil of turpentine 30, aniline color 5, Congo black 2, almond-kernel oil 8, *beeswax* 4, and *ozocerite* 10 parts. Leather is known to absorb this type of polish very readily, and the gloss resulting from its application to leather is well preserved.

Boot and Shoe Waxes and Finishes. The waxes and finishes used in the boot and shoe industry may be classed as (a) sewing and stitching machine waxes, (b) bottom and edge stains, (c) finishing waxes, and (d) shoe dressings. Thread is impregnated with so-called "machine wax" to obtain greater tensile strength, assure protection from damp and wear, and to fill the needle hole more readily. Although *machine waxes* generally contain little or no wax, since they are formulated largely from resin, pitch, and resin oil, it is advantageous to incorporate a hard wax such as *candelilla* to the extent of at least 3 per cent of the composition. In their preparation the resin (e.g., rosin) and pitch (e.g., burgundy pitch) are melted together with the wax, the oil is then added and mixed in, and the whole composition when thoroughly mixed is poured into water. The mass is then kneaded to press out the water and pulled to incorporate air. The average melting point is 60 to 70°C. A machine wax of the kind described is used by the shoe manufacturer for stitching.

For sewing, the thread may be impregnated with a mixture compounded from prepared machine wax 70, linseed oil 20, amyl acetate 5 and sassafras oil 5 parts. *Shoemaker's thread wax* sold in tins is usually compounded from rosin, *yellow beeswax*, and tallow. *Shoe wax stains* are generally prepared from blends of *carnauba wax* and other waxes, a suitable dye, and a large amount of thinner composed of turpentine and Stoddard solvent.

Antique Leather. Raised portions of the surface of the previously dyed and dried leather are given a coating with a "fatty resist," whereby the

deep portions can be dyed by means of a soft sponge, brush, or spray with a dye of the desired hue. The fatty resist generally consists of a mixture of wax and petrolatum. Any excess of dyestuff which may be present is then removed with a moist sponge and the leather dried. It is essential to use acid dyestuffs or basic colors which will not "bronze."

Finishing Waxes. "Finishing waxes" for bootsoles are made from wax which is hard and lustrous, such as *carnauba*, with *paraffin* or *ceresin wax* as a diluent. Instead of carnauba a 50:50 mixture of *candelilla wax* and a high-melting *hydrocarbon wax* (88°C, or 190°F—AMP) of carnauba hardness may be blended with lower melting point *paraffin* and a little *beeswax*. "Finishers black wax" is made from *carnauba wax*, *carnauba replacement wax*, rosin, carbon black, and an oil-soluble black dye.

"Liquid finishes" are liquid alkaline solutions of albumen or shellac, or are prepared from shellac dissolved in an organic volatile solvent, in which is incorporated a small amount of *carnauba* and other waxes. Pigment powders are used for suedes. Abrasives such as tripoli, powdered chalk, etc. are used in some of the shoemakers polishing waxes. *Montan wax* is used with other waxes, drying oil, and coloring agent in wax sticks employed for covering defects in leather.

Shoe Stiffner. In the making of box toes it has been customary to use a stiffner between the upper and the lining of a shoe and put the shoe in a heater to which moist heat is supplied. The stiffner is thus rendered limp and plastic, and the operator then inserts the prepared shoe in the pulling-over machine to carry out the pulling-over operation. Somewhat similar treatment follows at the toe-laster. The shoe stiffner when cooled must become hard, and rigid in the shape of the last, and hold its shape indefinitely.

According to Swett[159] a fabric material for box toes or shoe stiffening can be well prepared by impregnating the fabric with a composition consisting of a mixture of rubber, wax, and resin. *Montan wax* formerly found an extensive use in this art in the United States, but has now given way to various substitutes, including the synthetic waxes. *American montan wax* produced at Ione, California may be used satisfactorily. A varied group of waxes are said to be suited to the purpose, e.g., *carnauba wax*, *beeswax*, *shellac wax*, or the *microcrystalline hydrocarbon waxes*. The use of "*Alcowax*" 5 parts to *microcrystalline wax* (180/185°F—AMP) 95 parts makes a good replacement for carnauba wax in blended wax formulations. The wax or waxes selected are then blended with pracoumarone or coumarone-indene resin, and melted with rubber to produce the stiffner.

Swett[159] has given the following recipe: Nuba resin 45, colophony 30, rubber reclaim 15, and *candelilla wax* 10 parts. The ingredients are weighed out in a common vessel, heated to about 188°C (370°F) and simultaneously

agitated. The result is stated to be a homogenous molten, water-free, impregnant of a viscosity suitable for the saturation of a wide range of bibulous fabrics or fibrous bases such as felt, paper, textiles, and the like. Upon cooling the stiffner has the property of being thermoplastic when warmed, but rigid when cold, yet retaining elasticity.

Stitching Machine Wax. A high-speed lockstitch sewing machine, with totally enclosed mechanism and a needle automatically lubricated, is generally used for fastening the sole to the welt. The needle and shuttle threads are gummed or waxed, since uniformity and tightness of stitches is of paramount importance. The machine is heated by steam or electricity. A waxed or gummed thread is also used with the needle or hook on the heated sewing machine to permanently attach sole and insole to the lasted upper. The sewing machine wax can be prepared from *candelilla wax* 3, colophony 54, burgundy pitch 20, rosin oil 4, tallow 3, and heavy mineral oil 1, parts (also see p. 747).

Waxes as Softening Agents for Rubber. Materials designated commercially as "softeners" are used in rubber mixes prepared from natural crepe for the purpose of facilitating the processing on the mill, in the tubing machine, etc. There are numerous softeners, not necessarily waxes, used for the purpose, but in this field the softer paraffins, and the higher fatty acids, *stearic acid* and the like, play an important and special role. Stearic acid is used in truck tire and passenger tire stocks, e.g., 3 per cent in tread, and ½ to 1 per cent in carcass. *Paraffine* is used in addition to stearic acid in inner tube stocks, e.g., 1 per cent paraffine and 1 per cent stearic acid. About 2 to 3 per cent of stearic acid is used in heel stocks, and 2 to 3½ per cent in sole stocks. Paraffin and *montan wax* is also sometimes used as in the formulation of Monsanto Chemical Company for a tan sole stock: smoke sheet 100, zinc oxide 5, hard clay 200, montan wax 3, stearic acid 2, paraffin 1, antioxidant ("Santoflex B") 1, sulfur 3.5, accelerator ("L 60") 1.75, activator (DPG) 0.75, parts. The tread of a tire repair stock usually contains 2 to 3 per cent stearic acid.

Alternatives to *stearic acid* as softening agent in tire-tread and black-soling types of vulcanizates are *degras stearin*, *degras olein*, *distilled degras fat acid*, *neutral degras*, *degras magnesium soap*, *shale wax*, and a few others. The manufacture of GRS (buna-S) crepe from butadiene and styrene requires the use of several per cent of *stearic acid*. Rubber mixes are often made by combining the synthetic with the natural rubber crepe, whence not over one per cent of softening agent is needed, although an additional amount of paraffin wax or the like may be added to prevent sun-cracking, etc.

Wax as Mold Release of Rubber Goods. Wax is used as a mold release of mechanical goods, of foam rubber, and for the lubrication of tire

airbags, and of products made from latices. "*Carbowaxes*" find an extensive use for such purposes as well as polyethylene glycols. Shoe soles and heels, radiator hose, battery hose, hydraulic brake cups, and rubber mats may be molded with "Carbowax 4000" and "6000." The "Carbowax," 0.5 to 5 per cent by weight, is dissolved in water, and the solution is sprayed or brushed on the mold; the spray method is preferred. The application will last through a number of molding cycles. "Carbowax 6000" is better than "4000" for battery cases.

"Carbowax 4000" is used for mattresses, pillows, cushions, and automobile seats made of foam rubber. The high water solubility of the "Carbowaxes" insures ease of application and of removal from the mold surfaces when desired. They are good lubricants, and have high flash points. "Carbowax 4000" is sprayed on the molds either in aqueous solution or in a solution of about 90 per cent isopropanol and 10 per cent water. Generally 5 to 20 per cent by weight of the compound is dissolved in these solutions, and sometimes a small amount of clay or talc is added. After the solution has been sprayed on the mold, it is either dried with applied heat or allowed to dry by evaporation at room temperature.

"Carbowax 1500" is best in lubrication of latex products. Since styrene-butadiene synthetic rubber has a low tear strength the use of a wax release becomes more important than with natural rubber. From 2 to 5 per cent weight of "Carbowax 1500" is generally mixed into the latex compound, as for example in making latex dipped gloves.

Use of Hydrocarbon Waxes in Rubber. Both *crude scale* and *refined paraffin wax* are used in rubber molded goods, hose, baby carriage solid tires, etc. The wax is added directly to the rubber in the Banbury mixer. *Paraffin wax* is often used in rubber to a greater extent than is simply needed to prevent sun-checking, or sun-cracking, particularly where mechanical rubbers require a low friction surface, and may be used up to 5 per cent of the weight of the rubber, although pronounced blooming occurs in excess of 3 per cent. Paraffin is also used in rubber auto-topping and miscellaneous tubing of various kinds, e.g., windshield-wiper tubing, and in rubber flooring composition.

Microcrystalline hydrocarbon waxes can be effectively used in many elastomers to provide several desirable characteristics. These waxes were originally employed in the compounding of natural rubber, but have been found equally applicable to synthetic elastomers such as GRS (buna-S). They appear to be superior to other antisun materials to prevent sun-checking, although 40 to 50 per cent more microcrystalline wax than paraffin is necessary to cause blooming, but once a surface film has been obtained, greater protection is afforded. The film resists fracture during flexing and a continuous film can be maintained under all conditions to which the

elastomer is subjected. A preferred wax is one which has a melting point of 160 to 165°F (ASTM), a needle penetration at 77°F (ASTM) of 15 to 25°, a viscosity (S.U.) at 210°F of about 70 seconds, and a flash point of 460°F minimum. Microcrystalline wax when used to the proper extent in the elastomer composition acts as a lubricant to reduce tackiness. In an extruded automotive strip microcrystalline wax has been effectively used in addition to stearic acid, e.g., *stearic acid* 1 per cent, *microcrystalline wax* ("Syncera") 3.75 per cent.

Ceresin, like paraffin, has the peculiar property of working toward the surface of the rubber article much in the way that sulfur blooms. The ceresin used for this purpose is usually of an artificial make-up containing hard, medium, and soft waxes. Gaskets for the purpose of sealing glass containers, according to Parker[128], are made of a vulcanizate containing rubber crepe 30 to 35, stearic acid about 2, and ceresin 9 to 15 parts, together with a filler, like clay, and a vulcanizing agent such as sulfur. Waxes are also used as a protective material on colored rubber to prevent it from decolorizing or staining. Fatty colors of the lipoid type are intermixed with rubber and waxes of fatty acid, the latter preventing the penetration of the dye to the outer surface of the article.

Commercial Agents for Retarding Deterioration of Rubber. The use of paraffin wax to prevent the sun-cracking or sun-checking of rubber, and to better age-resistance has already been referred to. Davis and Blake[41] mention several types of hydrocarbons, or hydrocarbon-containing waxes, used in retarding deterioration of rubber. These antisun-checking waxes have trade names such as "Heliozone," "Sunproof," "Agerite Gel," and "Sunolite." Davis and Blake[41] state that waxes are of value solely for protection against deterioration by light or ozone. This is perhaps somewhat at variance with the generally accepted opinion. In the commercial agents we may have a combination of an antioxidant with the wax, which greatly intensifies the protective action of the latter. It is believed that the wax blooms out in a form saturated with the antioxidant, from the vulcanized rubber, and furnishes the best-known protection against chalking and sun-checking. The waxes most commonly used to obtain resistance to light and ozone, and inhibit the rubber articles from checking—that is, developing small cracks—under static atmospheric and "corona effect," are *paraffin wax*, *ceresin wax*, *microcrystalline wax*, and *ozocerite*.

The wax is customarily used to the extent of a ½ to 3 per cent, based upon the rubber hydrocarbons content, in many items containing natural or synthetic rubber (GR-S) but in larger proportions (3 to 5 per cent) for articles that are exposed near high tension wires and electrical discharges. The severe cracking that is experienced with many forms of electric rubber goods, by the higher concentrations of ozone, has become a baffling problem,

making it necessary to use the largest proportion of waxy ingredient in wire and cable insulations, electricians gloves, and items of similar nature.

Its general uses are for tire sidewalls, wire jacket and insulation, mechanical rubbers, footwear, garden hose, automotive specialties, and sundry goods. For white or pastel stocks the antisun-checking wax must be light in color.

Protective Wax for Neoprene. In neoprene formulations a high order of ozone resistance is imparted by the use of a protective wax, such as "Heliozone," with the antioxidants employed. Vulcanizates which contain the protective wax (3 to 5 parts) show twice as great an ozone resistance in the course of two years' aging than when the antioxidant in normal amounts is used alone. Wax, without antioxidants, provides little or no protection. Neoprene jackets are used for high voltage cables and require a fairly high content of wax and antioxidant to prevent so-called corona or ozone cutting. Waxes suitable for employment with neoprene are generally of the hydrocarbon type.

Wax in Latex Rubbers. It is often necessary to add a softening agent to a latex rubber in order to overcome its excessive toughness, and the commonly used softeners for the purpose are *stearic acid*, mineral oil, and *paraffin wax*. *Stearic acid*, when so used, is added to the extent of 2 per cent or more, on the basis of the weight of the rubber. The addition of stearic acid is effected through the preparation of an emulsion which is intimately mixed with the latex. To prepare the emulsion, 4 parts of stearic acid are melted with 1 part of oleic acid, and this melt is vigorously stirred into 5 parts of a potassium hydroxide solution of 0.12 per cent strength, after which 0.3 part of stronger ammonia solution is added with continuous stirring. The emulsification is best carried out at a temperature of 70 to 80°C.

In the production of colored rubber articles from latex by the dipping method, free stearic acid is used in conjunction with latex dispersions, by dissolving the stearic acid in a suitable organic solvent in which one per cent of the fatty coloring material is intermixed. A waterproof composition for proofing paper, fabric, etc., is made by intermixing an emulsion of a hard wax with latex.

Fully refined hydrocarbon waxes may be used to coat an aircraft covering that has been previously prepared by coating a fabric, under tension in stretching frames, with a rubber cement followed by certain latex coatings. The wax is of value as a sunproofing agent for the rubber surfaces. The art of preparing the aircraft covering is taught by Calvert in his U. S. patents[25].

Paraffine of a hard quality or *spermaceti* is used for coating synthetic violin strings just prior to application of the finishing coat of soapstone or

luster varnish. The strings of silk, wool, hemp, or other suitable cord material will have been impregnated with rubber latex, imitating strings of catgut, before coating with the wax.

In the manufacture of sponge rubber a hard paraffin wax can be incorporated in the frothed rubber-latex sponge so as to provide a good "snap," a high compression/weight ratio, and a low rate of combustion. The wax is emulsified before mixing with the natural or synthetic latex. [Rogers, T. H., U. S. Patent 2,594,217 (1952)].

Belt Dressings. Belt dressings for use on heavy-duty belts made of rubber or other material should provide oil for the belt and a tacky substance for traction. A belt treated with a dressing of the kind described will have an extended life, and there will be less strain on pulley bearings than if the traction were obtained by tightening alone. The two principal types of belt dressing are the "liquid type" and the more popular "stick type." According to Knuth[101a], power and V-belts are coated for improved traction and preservation with a mixture of chlorinated paraffin wax (65–75 per cent of chemically combined Cl) and a small amount of neat's-foot or castor oil. The mixture is heated to 110–120°C, agitated, and homogenized. It may be used as a viscous liquid or as a stick in a composition containing more paraffin wax.

A disadvantage in using the solid kind is that it imparts but little oil to the belt, the stick being commonly prepared with colophony and wax, with but a small amount of oily ingredient. Waxes, unless properly chosen, tend to lessen traction. The great advantage of the stick lies in its ease of application to the belt.

The liquid type of belt dressing is usually prepared from a combination of two or more of the following classes of oils: mineral, marine, animal, and vegetable. With the oils are mixed a small amount of oleo-resin (perhaps a combination of colophony and pine tar), a small amount of wax such as *anhydrous lanolin*, and a perfume oil such as oil of mirbane.

In a belt dressing of the solid type, that is, the dressing in the stick form, wax is customarily the chief ingredient. The waxes commonly used for the purpose are *beeswax*, *montan wax*, *woolwax*, and *scale wax*. In some formulations *stearine* is used, together with the wax, rosin, and a viscous oil such as castor oil. A tacky wax such as *petroleum wax* may also be used to advantage in stick dressings.

Tailor's Dummies and Dress Forms. Molded forms such as those for tailor's dummies can be made by draping a model, or even a human figure, with a pliable thermoplastic sheet material that can be readily molded or shaped while warm but which will stiffen when cooled so that it will hold its shape. The textile base is a double, or multiple-ply kitted fabric, so that the compound may deposit in the plies, between the plies,

and as a surface coating. The impregnating compound is a composition of wax, rubber, and resin. When the coated textile base material is steam heated it becomes limp, adhesive, and tacky, and can be made to conform accurately to the contour of the model. The composition is more durable than plaster of Paris, or papier-mâché and gummed tape for the purpose[108].

The trade name "Thermold" has been applied by the Lovell Chemical Company, Watertown, Massachusetts, to an expansible thermoplastic resin coated fabric of the kind described. After Thermold has been warmed by an infrared lamp, or by hot water (76°C), it is pliable for a long time but eventually stiffens. This unique property makes it possible to secure knitted dress forms from a human model; the dress forms are then removed with a parting agent such as a soapy film if the "Thermold" has been softened by dry heat along the fitting. The formed "Thermold" can be painted with a water-base paint, or shellaced and then painted; or sprayed with naphtha adhesive and flocked. The dress forms when finished are provided with close-fitting garments, in fashion garment manufacture.

A preferred recipe for the coating composition of the thermoplastic sheet material has been given by Lovell[108]: *candellila wax* 30, rubber 30, *beeswax* 10, synthetic resin or colophony 50 parts. The rubber is melted with the candelilla wax, and the rubber-candelilla mixture dissolved in molten beeswax-resin solution, at about 160°C (320°F) with thorough stirring. Synthetic resins such as *polystyrene*, *polyvinyl acetate*, *butyl methacrylate resin*, etc., may be used. "Thermold" softens and becomes plastic when heated above 55°C, an ideal temperature being 65°C, and remains in the plastic condition until cooled below 38°C (100°F), a property which lends itself to preparing the dress forms from a human model.

Ear Stoppers. Material for use in the manufacture of ear stoppers, tips of hearing aids, and the like is made of a patented composition: neoprene GN 100, light magnesia 4, stearic acid 1.5, "Permalux" 0.5, titanium oxide 12, iron oxide 0.4, *paraffin wax* 3, *anhydrous lanolin* 20, and zinc oxide 1 part by weight[167a].

WAX IN LUBRICANTS

Wax as a Lubricant. There are a number of ways in which waxes are used as lubricants: (a) in a solid cake or stick form, (b) in a mist or powdered form, (c) in a grease or liquid wax form, (d) in a slushing compound, (e) in a water emulsion, (f) as a foundation for grease overlay, (g) overlay of melted wax from dip tank, (h) as surface-active substance in drilling metals, (i) as an additive to compounds.

(a) Small objects may be lubricated by tumbling them with rough chunks broken from a solid cake of hard wax, in a barrel rotated at a slow speed for a period of time. When the objects are removed they will have a

slight coating of wax, a greasy feel, and a polished appearance. Cork discs for bottle caps have been treated in this manner, and so have small articles made of plastic.

Lubricating wax is used where oil or grease do not serve the purpose well, as on the dovetails and lock tongues of automobile doors. The lubricant is used in a stick form; it is not only useful on doors, but also on the hood lacings to prevent squeaks, rattles, and wear. A stick composition prepared by Rosen[142] is made by mixing together petroleum jelly 18, oil 18, mica 5, and waxes 59 parts. Waxes suitable for the purpose are *ozocerite*, *carnauba*, *petroleum ceresin*, *paraffin*, and the like. In preparing the stick the wax is melted and the oil added, also the finely divided mica; the entire mixture is raised to a temperature of 250°F and agitated, then allowed to cool to 160°F before it is pumped into the molds. The stick is hard and brittle but will become plastic and lubricate when pressure is applied. A stick composition may be made up of *paraffin* 50, *ozocerite* 33, *match wax* (m. 108°), and *carnauba* 2 parts, which is suitable for lubricating oven conveyor chains, etc.

American Grease Stick Company, Muskeegan, Michigan, molds the stick lubricants to a predetermined size for exact slip-fit in a slide container. The molded lubricating sticks are of a composition which will retain its oil content without softening or sweating, up to the temperatures approaching its melting point.

A brand of stick-type wax lubricant, known as "Do All Tool-Saver," is recommended by its maker for use on saw bands, knife bands, circular saws, hack saws, carpenter saws, twist drills, taps, reamers, spinning tools, etc. When used on paper or fabric drills, it prevents burning of the paper or fabric. A one-pound quantity is supplied in a handy "push-out" cardboard dispenser tube, measuring 11 inches by 2 inches. The lubricant is applied directly to the cutting edge of the tool or to the surface of the material that is to be machined.

(b) *Paraffin wax* can be used to lubricate objects by placing them in an oven where they are sprayed with the wax in the form of a mist. The intent is to spread a solid lubricant in a continuous film on the object which may be cardboard, molded plastic, metal, etc.

Paraffin, ceresin, or other waxes are used in spray machines designed to pick up molten wax from a small heated fountain and deliver the wax to the printed sheets of paper or metal in a very finely divided droplet condition before the sheets are stacked, in order to keep them apart and avoid smudging. This process is known as Grammer spraying. Metal sheets with lithographed designs can be sprayed by such a process and fabricated into closures for glass containers without injury to the design.

(c) *Sperm oil* which has been hydrogenated to a suitable lubricant for

the cold rolling of steel, or winterized *sperm oil* with the addition of *sulfurized sperm oil*, is used for the cold drawing of steel for making steel containers and other objects. Liquid waxes of this nature are also used for "sludging" carbon formed by mineral oil lubricants in heavy-duty mill applications. Jojoba oil (wax) may be sulfurized to the same extent as sperm oil and used as a base to fortify the lubricating power of lube oils.

Calcium, aluminum and sodium soaps are commonly used in ordinary lubricating greases. Sodium soap grease is not water resistant, and calcium and aluminum soap are not adequately heat resistant for the lubrication of wheel bearings. Greases made from strontium, barium or lithium soaps as metallic bases combine high melting point, water resistance, and good mechanical stability. Certain grease prepared from lithium soap and higher hydroxy fatty acids, such as *12-hydroxystearic acid* function well at a temperature as high as 350°F without unduly softening, oxidizing or separating (see All-Purpose Lubricating Grease, p. 644). Lithium "multipurpose grease" finds an extensive use for automatic and other purposes. Strontium and barium stearates disperse well in mineral oil and give fibrous greases of good stability.

(d) Petroleum waxes make suitable lubricants for a deep drawn metal stamping. The waxes used comprise one or more of the following: *paraffin, ceresin, slack wax, anhydrous lanolin*. The straight or blended wax is melted and a sufficient amount of high-boiling naphtha is added to form a stable slushing material on cooling. This mixture is then applied to the metal sheet in a thin layer by means of a felt swab, or by mechanical rollers before the sheet is punched or stamped. This method has replaced one where the felt swab was first dipped in benzine and then rubbed over a solid cake of paraffin wax before stamping the sheet of metal, such as tinplate or black plate.

(e) An example of a water emulsion suitable for lubrication is as follows: water 90.7, triethanolamine 0.67, *scale wax* 22.7, and stearic acid 2.35 parts by weight. The water and triethanolamine are heated together at 72°C. The scale wax and stearic acid are also heated to 72°C and then the two mixes are combined, and agitated until cooled to room temperature. This water emulsion may be applied to sheet metal by swab or felt roll to lubricate it for fabricating cans, toys, pans, etc.

(f) In lubricating shipways it is necessary to have a *base* lubricant and a *slip* lubricant (see Launching Lubricants, p. 759).

(g) Wax is used for treating gambrels and trolleys for conveying carcasses at Armour and Company and others in the meat-packing industry. The purpose is to eliminate grease and prevent drip-spotting of animal carcasses. A special wax compound of high melting point is used. The principle of wax lubrication may also be applied to other food industries

where materials are conveyed in troughs, racks, pails, or buckets, suspended from overhead trolley rails.

According to Parker[128a], the treating equipment consists of an insulated, gas or steam-coil-heated dip tank equipped with temperature control. The bottom of the tank slopes to a sump, and a gate valve through which sludge may be easily removed. Attached to the tank is a pump and filter for continuously cleaning the melted wax.

(h) In the cutting and machining of metals, the addition of a wax alcohol, such as *cetyl alcohol,* in a fraction of one per cent acts as a surface-active substance to kerosene or other mineral oil and facilitates cutting and drilling. The specific work of cutting annealed aluminum immersed in paraffin oil is greatly reduced by the addition of 0.25 to 0.50 per cent cetyl alcohol.

A paste of gasoline and *beeswax* can be effectively used in tapping aluminum. Wood for bearings is treated with a mixture of oil and *beeswax.*

Sweeping Compounds. Sweeping compounds are used in the sanitary maintenance of floors, particularly for sweeping large areas such as public and industrial plant buildings. The chief ingredients are such materials as fine sand, bran, sawdust, and the like. A few of the compound formulations employ waxes such as *paraffin wax* or *chlorinated paraffin wax. Beeswax* is efficient for the purpose but too expensive.

Mop Oils. Mop oils are made from mixed waxes, spindle oil, and turpentine, with or without the addition of mineral spirits, and are frequently artificially colored and scented. For example, to produce a mop oil, 3 parts of waxes may be dissolved in spindle oil 70 parts, and a mixture of 30 parts of turpentine with mineral spirits. The combination of waxes would be the same as that used in solid floor waxes.

Ski Wax. The ski or wooden snowshoe requires repeated treatment of its running surface so that it will glide easily in downhill progression and avoid back slippage in uphill progression. The Norwegians first apply a foundation of pine tar, and then wax hard, especially at the tip. The greatest use of ski waxes is for the military both in America and on the European continent. Three kinds of wax are chosen for the American army, and these are distinguished in use by colored labels—blue, red, and orange. These waxes are "dry snow wax" for very cold temperatures, "medium wax" for temperatures near freezing point, and "wet snow wax."

Before waxing, the running surface of the ski should have several layers of a good quick-drying lacquer, which can be applied with a soft brush; e.g., a liquid ski dressing according to Flint[61] is formed of celluloid ½ ounce, acetone ⅓ pint, shellac ⅙ pint and powdered graphite $\frac{1}{12}$ ounce. Waxing helps the ski to glide easily over the snow crystals; the drier the snow the less wax, and the wetter the snow the more paraffin needed. *Paraffin* prevents lumps of snow from forming on the bottom of the ski better than any

of the stickier types of waxes. Harper[79] states that paraffin is an especially fast wax on new or melting snow; it wears off quickly and must be applied very thickly.

Harper[79] states that below zero "Red Wax" can be used in a thin layer; above zero applied medium thick with a little paraffine; and above 32°F applied thick with a thick layer of paraffin. On iced, crusty, or granular snow it is advisable to use several layers of wax, e.g. "Red Sohm Wax," and paraffin, because these types of snow wear off the wax very quickly. A "Blue Wax" may comprise ⅔ wood tar and ⅓ hard waxes; a "Red Wax" ½ wood tar and softer waxes; and "Orange Wax" little or no wood tar, but rosin, and softer waxes. There is a considerable variation in the kinds of waxes selected for the make-up of the various commercial brands.

Wax is put on the ski with the palm of the hand or with a cork. A flat-iron does not allow the wax to penetrate the ski sufficiently and should not be used. According to Harper a torch is the best device for applying wax to skis. It is also handier to depend upon one wax, such as Red Wax, than to use three different waxes to suit snow conditions.

For cross-country skiing it is advisable to apply to the skis a foundation of tar or "Klister" instead of the lacquer foundation. The application is hot by means of a torch, and the foundation keeps the skis from sliding backward on the upgrade. When the snow is wet the cross-country runner may mix the wax with "Klister" instead of paraffin. A preparation of this sort is given in a Russian patent[14]. This wax is prepared by mixing rosin tar, turpentine, ozocerite, heavy mineral oil, and the sodium salt of rosin acids.

In using the U. S. Army waxes a thin layer of the Wet Snow Wax is applied over the Dry Snow Wax (Orange over Blue) for climbing purposes at sub-zero temperatures.

When using the Wet Snow Wax if there is a tendency of snow to stick to the wax, some Speed Wax is rubbed over it (Red over Orange). The Speed Wax is, however, not suited to climbing. American waxes are compounded from *microcrystalline wax*, *paraffin wax*, *beeswax*, and other suitable waxes. For fast running the stickier wax constituents which are valuable for climbing must be reduced to a minimum.

The U. S. Quartermaster Corps' specifications (BQD No. 85) for ski wax cover three grades known as E-1, E-2, and E-3. The E-1 calls for *Orange Wax*, for wet and corn snow, climbing, and running; E-2 calls for *Blue Wax*, for climbing and running (of different characteristics from E-1); E-3 calls for *Red Wax*, for speed, running, and sticky snow conditions.

The E-1 or Orange Wax is for climbing and running in dry snow at sub-zero temperatures. The wax must allow easy gliding in wet snow or corn snow; must allow climbing without back-slipping in corn snow, and in

powder snow at sub-zero °F temperatures on a slope of at least 18 degrees. It must rub to the running surface easily and rub out to an even layer with the palm of the hand or a cork at temperatures down to 32°F. The wax must wear at least as well in wet or corn snow as leading brands of "Klister." It must not emulsify. The wax must have a nearly white or transparent color, it must easily push up and down in tubes, and must not deteriorate in storage.

The E-2 or Blue Wax must allow easy gliding over all types of snow. It must allow climbing without back-slipping in powdered snow at temperatures between zero and 30°F on a slope of at least 15 degrees. It must apply easily outdoors as well as indoors and form an even surface without lumps when rubbed to the running surface. It must have good adherence to lacquered ski bottoms and wear well in any type of powder snow; an application should at least wear for a 10-mile ski run. It is expected that the color will not be darker than ivory, and that the wax will contain not less than 20 per cent of beeswax by weight.

The E-3 is designed for fast running in all kinds of snow. It must apply easily outdoors and form a smooth surface when applied over wet or dry snow climbing wax or over a lacquered ski bottom. It must wear at least twice as long as plain paraffin. It must be of a white or nearly white color, and shall not contain less than 8 per cent of beeswax by weight.

O'Neill has patented a ski wax lubricating composition in which the wax cake is made up from 1 pound of *paraffin* or *ceresin wax*; 0.5 pound of metal powder (e.g., copper, tin, zinc, bronze, and the like); and 136 grains of powdered tartaric acid crystals to serve as a dispersing agent and hardener. [O'Neill, E. C., U. S. Patent 2,610,150 (1950)].

Shuffleboard Lubricant. A mixture of wax and meal is generally used to lubricate a shuffleboard. *Paraffin* and *carnauba waxes* are dissolved in a solvent and added to the meal. The mixture is then tumbled, dried on driers, and cooled. To a cold mix of this kind Decepoli[43a] added organic plastic beads made of polystyrene, and later of methyl methacrylate; the beads were 40 to 60 mesh in size. Generally, about 10 parts of beads are thoroughly mixed with 90 parts of the waxed meal. More beads will make the gameboard faster, and less will make it slower. Decepoli claims that the composition with beads added gives a better and longer-lasting surface to the shuffleboard and also provides a cushioning effect between the colliding weights.

Launching Lubricants. The lubricants used for launching ships may involve as much as 50 tons of grease for the launching of a single large ship. The groundways are not greased until the launching period approaches. Any old grease left on them from previous launchings must be removed by torch. Although tallow, stearic, "soft soap," and boiled oil at one time

were used as launching lubricants the modern base coats are hard, waxlike materials whose purpose is to prevent the sliding ways from getting in contact with the groundways.

The waxlike materials must be melted and applied in liquid form to the ways, usually to a thickness of ¼ to ½ inch. Generally speaking the shipyard is equipped with a kettle in which about 15 barrels of base coat can be melted at a time. The base coat is applied on to the ways, following heating by torch. Later, electrical heating irons are used to smooth the surface; this operation is called ironing. This is followed by the application of a slip coat. The ship itself is supported by shoring, cribbing, and keel blocks, ready for release at the launching.

Molten paraffin wax from a kettle held at a temperature of 200 to 250°F is applied to the preheated shipways as a base foundation, and then a grease (ship launching grease) made from oil and *calcium stearate* is applied over the surface. In order to secure a good adhesion of the base coat to the wood the blocks may be coated with a thin layer of lubricant prepared from *paraffin wax* 55 to 75, and *petrolatum* 45 to 25 parts, which mixture is applied at 120 to 130°C (248-266°F), while the remainder is added at 100 to 110°C (212–230°F) to form the base. Another procedure calls for applying the paraffin-petrolatum wax mixture at 130 to 150°C (266–302°F) to the blocks, then applying a mixture of paraffin wax 30 parts, petrolatum 70 parts as a "middle" over the lowest pressure layer, and for the top layer green soap and a linseed oil-petrolatum compound, covered with a very thin (1 mm) mineral oil layer.

WAX IN THE LUMBER INDUSTRY

Hygroscopicity is one of the chief disadvantages in the use of wood. Shrinkage and swelling, checking and streak staining after the timber is cut may be overcome by impregnating the lumber with wax. The fresh cut logs can be painted with wax emulsion, in the forest. Wax is also used in impregnating flat, thin strips of wood, when they are used for storage battery separators, hallocks for berry packing, etc. Wooden tanks for use in chemical industries are often impregnated with wax. The waxes most commonly used are paraffins or microcrystalline waxes, or blends of both.

Treatment of Lumber. The highly prized woods, such as walnut for gun stocks, and dogwood for shuttle blocks, are prone to check at the ends and develop streak stains if not protected by wax while the lumber is green. Lumbermen are provided with wax emulsion to paint the ends of the logs immediately after the timber is cut in autumn. A loom, which is a frame or machine for weaving thread, or yarn, into cloth by crossing threads called the "warp" with others called the "woof," has "picker sticks" made of hickory, and "shuttle blocks" which must be made of an extremely dense,

wear-resistant wood, such as dogwood, *Cornus florida* L., of shade-grown slow growth. The lumber without checks is very expensive—about $1750 per 1000 board feet. The ends of the logs can be well sealed with a heavy wax emulsion of the soap type. *Microcrystalline wax* is far more protective than paraffin wax for this purpose and the concentration of the emulsion should approach 50 per cent solids. An emulsion of this type is "Ceremul M" of the Socony Mobil Oil Company.

Impregnating Wood with Paraffine. Wood may be impregnated with paraffine by placing it in a tank, which is then tightly sealed. A vacuum is drawn by means of a pump to exhaust the air; then the molten paraffin is run in until the wood is completely immersed, and after 10 or 15 minutes an air pressure is applied to further drive the paraffin into the pores of the wood. The structure of wood does not allow more than a good surface coating. Eberlin and Burgess[52] found that wood should not be dried before immersion in the melted wax. They advised placing the wood in a tank of the wax heated to 71°C (160°F) and then raising the temperature gradually to 105°C in about 30 minutes. Then the temperature is slowly raised, during 3 to 4 hours, to 135°C. The wood is transferred to another paraffin bath at 71°C; after 30 minutes it is removed, and its surface wiped free of excess wax.

Under the aforesaid conditions of treatment in an open tank, spruce wood will absorb 124 per cent paraffin, when using specimen board 11 x 100 x 92 mm. Wiertelak and Czarnecki[174] at the University of Pozman, Poland, found 93.2 to 97.8 per cent absorption took place in two hours. The wood retains a considerable amount of moisture. The paraffin-impregnated wood resists comparatively well the action of sulfuric acid solutions. However, in two months' time the paraffin-impregnated board may take up as much as 26.5 per cent of storage battery acid. If dilute sulfuric acid solutions are to be handled there is less absorption, and the paraffin-impregnated boards may be safely used in building tanks and containers.

WAX IN MATCHES

Historical Aspect. The earliest use of wax in matches appears to have been in an impracticable contrivance known as the phosphoric taper, which dates back to 1781. This was of wax, enclosed in a sealed glass tube, at the end of which was a fragment of phosphorous. After the tube had been dipped in warm water, the end remote from the phosphorous was cut with a file; the taper was withdrawn, with some of the phosphorous adhering to it, and spontaneously inflamed.

The first useful friction match was invented in England by an apothecary, John Walker of Stockton-on-Lees, Durham, in 1826[47]. The tips were made from a composition of potassium chlorate, antimony sulfide, and starch,

as a binder. The method of striking to obtain fire was to draw the splinter or splint tipped with the composition, over a piece of sandpaper. These so-called "friction lights" or friction matches were supplied in tin boxes, together with a piece of folded sandpaper. Imitations of Walker's matches appeared on the London market in 1829 and for a few years thereafter, under the name of "lucifers," but these likewise were difficult to ignite. To increase the flammability of the splints they were sometimes dipped in hot tallow, resin, and wax, but most of the splints were dipped in sulfur to make them readily flammable.

In 1832 match boxes were made with special striking surfaces, a development which was also made possible by the improved chemical composition of the tip, namely a mixture of potassium chlorate, antimony sulfide, sulfur, and gum arabic. The strike-on-box matches were sold in England and abroad under the name of "congreves," after Sir William Congreves, inventor of war rockets at that time, and they replaced "lucifers." In 1831, a Frenchman, Dr. Charles Sauria, of St. Lothair, replaced the antimony sulfide component of the match tip by phosphorous, thus improving the practicability of the friction match, which became now known as the "phosphoric friction match." In the United States a patent was granted to Alonzo D. Phillips for the invention of a "strike-anywhere" match, whose ignition composition was a mixture of yellow phosphorous, sulfur, chalk, and glue. The wooden splints dipped in sulfur and tipped with the composition ignited readily, the flame being transmitted to the splint with the sulfur acting as a carrier. The use of phosphorous sulfide instead of phosphorous was proposed by Puscher, of Nuremberg, in 1860. Haunan and Mills of England, in 1882 proposed a friction match paste containing wax and resin.

Fire hazards with phosphorous friction matches led to the preference for a "safety match," in which the flammable portion of the match head composition, chiefly amorphous phosphorous, was affixed to the side of the box. This early invention of 1844 is generally credited to Pasch of England, even though it was not placed in commercial manufacture until 1855, and then in Sweden by Lundstrom. The Swedish safety matches had the oxidizing mixture on the match heads, and red phosphorous on the box.

Phosphorous sesqui sulfide (P_4S_3), which is nonpoisonous, was introduced in match manufacturing establishments in Paris in 1898 to replace phosphorous. Its use in the United States followed thirteen years later for "strike-anywhere" matches. The introduction of wax for treating wooden stems, or splints, does not seem to have taken hold until 1861, when Letchford of England recommended using melted *paraffine*, or a mixture of *paraffine* with *stearine*, and *japanwax*, as a substitute for sulfur. With the substitution of paraffin wax for the sulfur as a flame carrier, and with the

formula for the match heads carrying more potassium chlorate and less phosphorous, a so-called "parlor match" was developed, wherein the irritating fumes of burning sulfur on the splint and phosphorous on the tip were eliminated. The use of colored paraffine was proposed by Bell in 1891. About 1905 the so-called double-dip match supplanted the parlor match. The double-dip match can be ignited readily by friction, since its tip contains a large percentage of phosphorous and the flame is transmitted to a somewhat less active first dip or bulb of the match and thence to the paraffined splint.

The use of fire-retardant chemicals for the treatment of wood splints dates back to 1879, and has now become a general practice with the American match manufacturer. A solution of ammonium sulfate is commonly used for the purpose of impregnating the splint; the splint is then dried and paraffined.

Paraffin wax has now become universal for the coating of match splints, and its consumption in the United States approximates 8,000,000 pounds per year.

Wax Treating Wood Splints. In order to spread the flame rapidly from a burning match head to the stick it is necessary to treat the splint with a highly flammable substance, such as sulfur, phosphorous, or wax. The treatment of the wood splint with *paraffin wax* has survived all other methods as being the most practicable one. Match splints, therefore, regularly receive a paraffin treatment prior to the application of the ignitive compound at the end. This method of paraffin treatment is automatic in the modern type of match machine equipment. The splints are placed in a hopper, and by means of a joggling mechanism and plungers, are inserted into the so-called match plates. These match plates have perforated holes, usually in two rows abreast, to receive and carry the matches, and form links of a continuous chain, or endless belt. The chain travels slowly and conveys the splints, tips downward, over a hot plate, and through a steam-heated bath of melted paraffin wax held at a temperature of 220°F. From the paraffin bath, the splints are conveyed over a dipping roller, which revolves in a trough or fountain containing the match-head composition. From the match paste trough the matches pass over a series of large diameter drums or carrier-wheels, where they are dried by currents of air. After having traversed the carrier-wheels, the dry finished matches reach the starting point of the endless chain, where they are ejected by plungers to meet the holes in the match-plates, and are then packaged by suitable box filling equipment.

American Manufacture of Matches. In American manufacture of stick matches of the strike-anywhere type the procedure is substantially the same in principle as that described above. Blocks of three-year-aged,

straight-grain white pine are hand fed to the "splint" machine. The hollow "splint knives" of the match machines cut 60 match splints at a single stroke. Making 400 strokes a minute, it cuts and places each splint into individual holes in the carrier plates. The splints, fixed in the plates of a special conveyor, pass through a dip of anti-afterglow solution, are dried by heaters, and are subsequently dipped into *paraffin wax* to maintain flame after combustion. The splints now receive their first bulb-forming compound, by passing slowly over and into the "dip" roll. After fan-drying, a second dip is made to form the "tip." The completed bulb is now dried and receives its final bath to assist proper hardening. The finished but damp match undergoes a 45-minute drying and hardening journey over carrier wheels through accurately controlled temperatures. The dried matches with still slightly damp tips (to reduce fire hazard) are punched out of the carrier plate into a vibrating trough. Mechanically shaken into uniform position, the boxing machine half fills each approaching container. The container is automatically reversed and the filling completed with matches lying in the opposite position. Straps and covers are mechanically applied and the boxed matches proceed for the packaging in cartons and subsequent shipment. A single match-making machine at the Oswego, New York, plant of the Diamond Match Company turns out 24,000 strike-anywhere wooden matches a minute, taking 65 minutes for the complete operation from block to box, as described by "Oil-Power" (Socony Mobil Oil Company)[34b].

Fairburn[67] proposed the treating of match splints to render them combustible but nonglowing by dipping the splints into a flowing stream of molten paraffin in which boric acid and alum, or other fire retardant, is suspended. Customarily the splints are impregnated with ammonium salts, preferably monoammonium phosphate, for the purpose of preventing a glow of the stem after extinguishing the flame. The splints must be dried before putting them through the paraffin treatment. The preferred wood splint is the round and grooved stick, which after paraffining receives a double dipping; first a dip to give the match the bulb, and a second to form the "striking eye" which is usually of a different color. The invention is credited to the Saginaw Match Company. In the double-tip match the striking-eye has the more ignitable composition. Double-dipped matches in the process of manufacture are best dried after the first dipping in an atmosphere of 30 per cent humidity or less at 38 to 65°C, and after second dipping at 50 to 65 per cent humidity and 20°C temperature.

What is commonly known as *match wax* is essentially a low-melting, crude scale paraffin. The melting point may be as low as 110°F. Its color range may be from pale yellow to +10 (ASTM D-156) and oil content should preferably be below 5 per cent (ASTM D-721). Some match manu-

facturers prefer a melting point of 124 to 126°F, and oil content below 3 per cent. Without the wax treatment the ignitive head would not adhere tightly to the stick. Higher melting paraffins can be used, but prove more costly. The large manufacturers purchase their paraffin in tank car lots and store it in steam-heated, insulated tanks to keep it in a liquified condition, so that it can be pumped directly to the match machines as needed. Emphasis is placed on keeping the temperature of the wax bath at 240°F or above to preclude the occurrence of a match bulb flying from the stick when the match is struck, which will happen when a wax fails to penetrate the wood splint.

Wax in Match Heads. According to Crass,[39] a number of match manufacturers incorporate a small amount of *paraffin wax*, that is, about 1½ per cent of the total batch volume, in their bulb composition (not the striking-eye) for the match head. The addition of paraffin has the effect of producing a smooth, quiet, burning match, the flame of which is generous and billowy in character. In making such a composition the hot melted wax is added to the hot glue solution before the addition of the other ingredients, and thoroughly mixed in order to get adequate dispersion of the wax in the glue. The prepared composition is velvety and has a dull luster which is carried over and imparted to the finished match head, thereby increasing the attractiveness of its appearance. However, Crass further states that the value of such wax additions is open to question because of their tendency to reduce the bonding efficiency of the glue and to make the match head brittle and more susceptible to crushing and flying, when it is struck. Such matches also tend to soften at elevated temperatures. Resistance to moisture is improved, however, which is of distinct value under certain climatic conditions.

Swedish Matches. Swedish matches are generally recognized as safety matches prepared from wood veneer of poplar, cut by means of a guillotine knife, which causes them to have a square cross section. The splints of wood are kiln dried and the end to be covered with the ignitive compound is dipped in a solution of paraffin in benzene, whereupon the splints are again dried. They are then dipped in the match head compound which is of such a consistency that only small drops adhere to the splint. The compound is usually made up of potassium chlorate, red and/or yellow lead oxide, antimony trisulfide, potassium chromate, gum arabic, *paraffin wax*, and water. The brown color of Swedish matches may be ascribed to the presence of the antimony. The paraffine is generally rubbed up with the antimony and then incorporated in the compound.

Formulas for the compound are modified in order to secure quick ignition and quick flaming, or retarded flaming, if desired. The striking surface on the box employs no paraffin. It is a compound of amorphous phosphorous,

sifted iron pyrites, pulverized glass, and a little gum solution; or a compound of similar character. The most important Swedish match manufactories are those of Jönköping, such as the Vulcan factory at Tidaholm.

Sulfur Matches. Sulfer matches date back in origin to about 1700 A.D., a century before the advent of boxed "lucifers." The ends are dipped into melted sulfur, stearic acid, or wax, and then into a compound of potassium chloride, antimony sulfide, and glue water. A sulfur match is of the strike-anywhere type and when ignited has a long-burning match head.

Parlor Matches. Parlor matches are strike-anywhere matches which have a lustrous colored match head. In the original Austrian type of "de-luxe" or parlor match, the match head was treated by hydrogen sulfide, which gave it a silver appearance. The use of colored lacquers for coloring the lustrous heads began in 1879. In parlor matches the sticks are soaked in *stearic acid*, and then dipped in the match-head compound of phosphorous, gum, water, fine sand, and red lead; or other suitable composition.

Wax Matches. Matches with wax stems were known in England as "vestas" and date back to 1832. In the same year Siegel, in Vienna, combined resin with wax to produce a firmer match stem. "Vestas" were first produced on a commercial scale in 1836, by Savaresse and Merckel in Paris, who used a composition consisting principally of *stearic acid*. Later, in England, *stearic acid* and gum copal or gum damar proved to be a satisfactory composition for the stems. The use of *carnauba wax* to harden paraffin for the same purpose was proposed by Childs, of England, in 1862. Strips of veneer, with one or more threads applied longitudinally, form the case patented in England by Stedman in 1906.

Wax matches are produced from long wax tapers which are then cut off at match lengths. The wax receives its support from strands of cotton, strips of bristol board, twisted paper, threads of jute, or other suitable core material. The wick material is drawn through the wax in a steam-jacketed tank, and thence through perforations in a d· w·-plate, and afterwards over a drawing drum, then back into the wax tank, and then over an opposite drum, and so on, until these alternate windings produce a sufficient coverage of wax so that the taper can pass through the holes in a suitable gauge plate; finally it passes through a heated perforated plate which polishes the taper. The taper is then cut to the match length by a wax machine of a continuous type (as that of the Diamond Match Company) which delivers the stems to the dipping roller for application of the match-head compound, and then dries them over carrier wheels.

Tiny *safety wax matches* 3 cm long and 1 mm in diameter with a jute or other very long fiber core are manufactured in scenic view paper boxes, 5 x 4 x 1 cm size, with pull tab and striking surface, by the S. A. Fäbbriche

Fiämmiferi-ed-Affini, Milano, Italy. There are 100 matches to a box, which has an open-cover drawer with a snap-back reclosure. Despite the tiny size with the greater volume per package than the book match, they burn as long and more uniformly.

Book Matches. The patent on book matches was issued to Joshua Pusey of Philadelphia, Pennsylvania, September 26, 1892. Book matches carry a preplanned form of advertising which makes it possible for the manufacturer to distribute them through many channels with little or no cost to the consumer. The match manufacturer profits by selling space on the book. Book matches are of the safety type, striking only upon a prepared surface, a strip of striking compound (red phosphorous) being painted on the exterior of the cover. The striking strip is then bent upwards and the comb section sewed by wire to the cover. There are twenty matches to each book.

In the manufacture of the combs large rolls of chemically treated paper pass through dies in a machine to emerge as "combs" of stems, the width of ten books. The die that cuts the "stems" and then forms the comb performs its function so that each stem is completely separated as to permit individual heads to be formed in the subsequent dip baths. The undipped combs are inserted by machinery into chain-like racks which will carry them through the dipping and drying processes. The stems of the comb are carried through dip baths which apply the *paraffin wax* that bears the flame and the head with ignitive compound that helps to initiate combustion. Generally there are two comb sections to a book. Carried by big chain-like conveyors, the completed match combs are dried and brought to the cutters. Comb and cover meet at the "stitcher" where they are stapled into the complete book, boxed, wrapped, and cased.

The production in the United States of book matches is 12.5 billion books annually, equivalent to 250 billion paper matches. The output of book matches in recent years has more than doubled that of stick matches. A paraffined paper pulp stem will produce a billowy flame quite similar to one made of wood.

Many of the factory operations in making book matches were originally covered by a series of patents granted to Criswell, of New York, in 1911. Ellern[52a] claims that the rigidity of the paper match is increased to that of the wooden match of equal dimensions or from 150 g to 520 g breaking strength, by impregnating the match splints at 240 to 260°F with a solution of *white paraffin* 67, limed rosin 15, *hydrogenated castor oil wax* 7, and *carnauba wax* 11 parts.

MOLDING AND CASTING IN WAX

Techniques of Molding and Casting. Molding and casting are processes of reproducing an object in form, and often texture and color, iden-

tical in appearance with the original from which the copy or reproduction is made. Molding and casting as a unit is referred to as "moulage," although this term sometimes designates the finished cast or positive.

When reproducing an object such as the human face, the face (after greasing) is covered with a thin layer of wax, by spray or by brush, and over this an outer shell or case of plaster of Paris is built up as a supporting medium for the wax impression of the face. This impression is called the mold or negative. When the mold is removed from the face, it is filled with a suitable substance to make what is known as the cast or positive. If an entire human head is to be molded, two profile molds are made, which are later fitted together.

Materials for Making Molds. Many materials, such as plaster, agar, composition glue, sulfur, rubber, baked sand, terra-cotta, etc., are suitable for making molds. Wax, however, is particularly applicable to molding small or delicate objects such as fruit, flowers, coins, medals, or the hands and face.

Artisans find through experience what appear to be the best waxes or wax compositions for each purpose. For example, rosin 1, *white wax* 3 parts, is suited for casts. However, for molding of the face or hands a wax of a different composition is used. The wax must be tolerated by the skin, and naturally must be one of low melting point. A wax mixture known as B-11, described by Golden[70], is composed of *paraffin* (m. 51.7°C) 55, *bayberry wax* 20, *carnauba wax* 5, and *stearic acid* 20 parts. This mixture has a melting point of 53°C, and is sprayed on the greased face, or other object, by means of a De Vilbis type CB spray gun, at a pressure of 4 to 6 pounds. The first layer acts as an insulator for a second layer, about one-half inch thick, which is applied by spatula when the wax is in a congealed state. Small rubber ice bags may serve for chilling the wax. It is customary to support the mold with a sufficient quantity of plaster of Paris.

A wax composition for application with a camel's hair brush instead of a spray is as follows: *bayberry wax* 50, *paraffin* (m. 51.7°C) 25, *stearic acid* 25 parts. This mixture has a suitably low melting point, 42.0°C.

To cast a plastic positive in a plaster negative it is necessary to use some separating medium between the two. *Yellow beeswax* 1, carbon tetrachloride 9 parts, makes a desirable separator. *Paraffin* 1 dissolved in benzene 5 parts has also been recommended.

Separating Mediums for Moulage. If the mold is plastic and the cast is a wax composition which is to be removed from the mold, this can be accomplished by soaking the moulage in a sodium or potassium citrate solution. Sometimes potato starch is used with the plaster so as to enable the mold to disintegrate.

To separate wax from plaster, the plaster mold is soaked in warm water

before pouring or painting on the wax. It is then soaped with shaving soap or other suitable lathering soap, the excess wiped off with a brush, and the mold polished. A thin film of soap facilitates easy separation of the wax positive from the plaster mold.

Clarke[30a] states that the best positive material for producing a lifelike reproduction of flesh is a composition having a resin and wax base, and resin-wax compositions are of great value for the casting of medical and biological subjects. Clarke has laid down definite specifications for resin-wax compositions that involve plasticity, melting point, shrinkage, etc.

Positive Impression Compositions. Waxes for positive impression compositions usually comprise suitable mixtures of waxes, mineral clay, and possible resin, and starch. Starch is of value where water is used to assist removal of the positive from the mold in moulage practice. According to Clarke[30a], positive wax impressions may be prepared by the formula of Douglas, which is *white wax* 4, *paraffin* 3½, talcum 2, cornstarch 2, and *yellow beeswax* ¼ parts; or by the formula of Ziskin, which is *refined paraffin* 22, *pale carnauba wax* 2, *beeswax* 1, and *dark carnauba* ½ parts. Carnauba wax itself has high cohesive and low adhesive properties, but is of value as a hardener and as a "booster" of the melting point of the composition. Clarke found that the introduction of a microcrystalline wax of high penetration value such as "*Petrowax*" was particularly advantageous as a means of preventing the cracking of positives.

Casts are usually stengthened by the use of cotton, wood, jute, hemp, cheesecloth, or burlap, to give bulk. These materials are dipped in the positive composition and applied back of the cast after it has reached about ⅛ inch thickness.

Clarke[30a] gives the following resin-wax formula: "*Parowax*" (m. 56°C) 5, colophony 10, *carnauba wax* 1, talc 4, and zinc oxide ¼ parts. A harder wax-resin formula for pouring into the mold, but not for brushing it, is as follows: "*Parowax* 8, *carnauba wax* (*pale*) 2, *beeswax* (*yellow*) 1, rosin WWW 2, and turpentine ⅕ parts.

Use of Wax Matrix in Printing. Printed pictures, etc., are treated so as to resemble oil paintings by the Thompson process[163]. The printed pictures are embossed by means of an electrotype surface obtained from a wax matrix prepared in the following manner. A copy of the picture is made transparent (by an oily liquid) and is fixed downwards in front of glass or any other transparent sheet. The back of the print is then covered with wax, and by means of a wire, or bristle brush, marks are made on the wax by following the lines of the reverse picture seen through the wax. It is necessary to transmit strong light from a source of illumination back of the glass.

An electrotype is made from the wax matrix. This electrotype is used to

emboss the prints from the back. A reverse electrotype must be made from the positive it is is desired to emboss the prints from the front. Alternatively such a reverse electrotype can be made from a negative matrix by fastening the print face downwards on glass and coating the glass (instead of the print) on the other side with wax, or by securing the print face upwards and coating the face of the print. Where the canvas on the original picture is shown, an imprint on the wax may be obtained by pressing canvas upon it.

Lost Wax Art Process. The "lost wax art" is an expression given by Benvenuto Cellini to an ancient craftsmanship by goldsmiths which was revived by him in the design and sculpture of his many marvellous works of art such as the gold medallion of "Leda and the Swan." The Italian artist, metal worker, and sculptor was born in Florence in 1500. In modern times the "lost wax art" has been adopted in the jewelry trade for duplicating rings, bracelets, and brooches of intricate design. The models of Cellini were most probably sculptured in *beeswax*.

In the "lost wax process" the object is first sculptured in wax; a thin coating of wet clay is then plastered around, and the object backed with clay to form the molds made with a hole in the top and bottom. The clay is allowed to harden and then the entire form is subjected to a sufficient amount of heat to melt the wax until it runs out the lower vent, leaving a cavity of the required shape. The mold is heated to about 1600°F or above to drive out retained moisture and burn out residual wax. The hot metal is poured into the top vent, the bottom one allowing for the escaping of air. After the metal has hardened, the clay is broken away from the outside, thus leaving the cast object. Metal parts are cast in brass, steel, zinc, or lead alloys.

Quantity production of many precision parts for electrical equipment, ordnance, turbine blades, and aircraft instruments is now dependent upon the art of precision casting, which is a slight modification of the above-described process. Precision casting affords the means of producing parts where the specifications call for extremely close tolerances; these can be held without the great expense of machining, requiring only finishing by blast or tumbling. (see Wax in Precision Casting, p. 771, and also Microcast Process, p. 771).

Wax in Precision Casting. An important art has developed in precision casting of small mechanical parts of metals and alloys, particularly of ferrous metals. This art in principle is similar to that used in making certain nonferrous metal or alloy castings by dental laboratory technicians, jewelers, and manufacturers of intricate surgical instruments. A wax model is made of the small part, making due allowance for shrinkage in casting, etc., and a ceramic mold is formed around this wax model. The wax is then melted out to get the exact contour, and the molten metal poured in the ceramic mold.

In the mass production of mechanical parts a *master pattern* or die is required to make repetitions of the wax model. This metal die is machined or cast to match the pattern with precision. Hundreds of wax forms are cast in the die, and these may be assembled in suitable arrangements so that they are interconnected by sprues. A larger sprue is formed to connect the system to the outside. The assembly of interconnected wax forms is coated over or *invested* with plaster of Paris or a sand-magnesia mixture. After the *investment* is set it is heated to melt out the wax, and then baked. The wax is reusable. The metal parts can then be cast in the finished mold, and the mold centrifuged to eliminate gas pockets and to secure uniformity. After cooling the complex form is broken up and the sprues are cut off.

Precision casting is of considerable value where the metals have too high a melting point for die casting, or where the shape is too intricate to produce it in a steel mold with the aid of hydraulic compression followed by subsequent sintering as in powder metallurgy technique. It has an advantage over the ordinary casting method in producing a cast part which has an exceptionally good surface, sharp outline, and dimensional accuracy.

The type of wax used is one which has a low coefficient of expansion, is of low viscosity, and can be easily ejected from the master pattern. A high melting paraffin (e.g. 132/135°F (ASTM)) is of that nature, although the preferred wax is usually a mixture of two or more waxes, such as petroleum ceresin (180/190°F) 40, paraffin wax (132/135°F) 40, and vegetable wax (candelilla) 20 parts.

A pattern composition for investment casting is given by Weston[173a] and consists of *stearic acid* 8, *aluminum stearate* 0.25, and *magnesium stearate* 0.25 parts, with or without the addition of polyisobutylene as a plasticizer. It is claimed that such a composition has high fluidity at a melting point of about 125°C, and does not require high pressures during molding. The isobutylene may be incorporated in the mixture by the use of "Tervan 2800" or like concentrate containing polyisobutylene of the lower molecular form. The chief purpose of the polyisobutylene is to reduce shrinkage of the casting wax on solidification. Shrinkage is almost entirely eliminated, according to Weston, by the use of 13 per cent of polyisobutylene, although the composition is not as fluid as when using this additive to the extent of 3 to 8 per cent.

Microcast Process. The name "Microcast Process" is the precision investment casting technique for the casting of a nonmachinable colbalt-chromium-molybdenum alloy known as "Vitallium," with a melting point in excess of 2500°F, as it is practiced by the Austernal Laboratories, Inc., New York. R. W. Erdle and C. H. Prange are credited with originating Vitallium microcastings in 1929. The microcasting method is substantially the same as that described previously (see Wax in Precision Casting, p. 770). The steps involve the preparation of an injection die, wax injection,

pattern removal, ganging patterns, primary dip, mold assembly, mold investing, mold heating, casting setup, casting, gate removal, and inspection. There are instances where a casting had 104 microparts for economy production, or where 28 spindles could be cast simultaneously for efficient production. The method is used for quantity production of castings of S.A.E., N.E. Stainless and Tool Steels as well as "Vitallium." The method can also be employed in microcasting bronzes, brasses, aluminum, and the precious metals.

Some of the commercial uses of microcastings have been for the blades used for turbo superchargers on U. S. Navy combat planes; buckets and compression vanes for "Boeing" turbojet engines; spindles for "Zenith" silent-speed record changers; stainless steel valve and pump parts; parts for soda fountain dispensors; tiny port plates; gate wedges; gears; levers; rocker arms; "Sportster" camera lens plates; and the shaft of "Shavemaster's."

Feagin[59] proposed adding a polymerized vegetable oil, such as polymerized cashew-nut-oil or other drying oil, with or without resin to the molten wax. By using 10 per cent or thereabouts of the polymerized oil with waxes such as beeswax, palm wax, ceresin wax, etc., the resultant thermoplastic composition is moldable, form retaining, and adapted to being invested in refractory mold material and completely eliminated therefrom by the application of heat. Feagin particularly recommends it for casting procedures which are employed in making dentures, jewelry articles, and similar items of detailed and irregular contour. Waxes other than those referred to that are employed singly or in combination in the polymerized drying-oil-wax thermoplastic composition are *bayberry wax*, *candelilla wax*, *carnauba wax*, *ouricury wax*, *microcrystalline petroleum wax*, and *sugarcane wax*.

Thermoplastic Wax Material. A thermoplastic material of Westinghouse Electrical Corporation, suitable for making patterns, is made by combining *candelilla wax* (about ¾) and a reaction product (about ¼) of rosin, glycerol, and a drying or semidrying oil. Ester gum and the oil are heated together in suitable proportions to produce the desired viscosity; or rosin and glycerol may be heated directly with the oil. Alternatively rosin, and an unsaturated fatty acid and the proper amount of glycerol, may be used. [Willis, H. B., U. S. Patent 2,467,796 (1949)].

Molding Material for Die-cast Objects. To molten *candelilla wax* maintained at 250 to 300°F is added 1½ per cent of its weight of soda ash, whereupon the wax froths and darkens in color. The mixture is then heated to 400°F and an equal amount of ethyl cellulose in granular form is incorporated. When the ethyl cellulose is dissolved or well dispersed a filler, such as wood flour, cotton flock, or carbon black, is added to the extent of

5 to 10 per cent by weight of the mixture, which is maintained at 400°F until smooth, then cooled and rolled into sheets ¼ inch thick. It may be ground for use in die-casting machinery where, according to Lovell and Straw[108b], the patentees, it shows excellent molding qualities under 200–700 pounds pressure followed by quick hardening. *Carnauba* or *montan waxes* can be similarly used.

Wax Portraits. The ease with which wax can be worked has insured its use throughout the ages in modeling. Modeling in wax, says Bolton[16], has always been done for one of two reasons: either as a means to an end or as an end in itself. During the Renaissance, doubtless, wax was used for both reasons, but more often as a means to the end. The bronze medals of Pisano owe their delicacy to the fact that they were first modeled in wax. Wax objects of art may be grouped into three classes: statuettes, allegorical subjects, and portraits in relief. The first class appears to have no examples in America, and but few in Europe. The second class, allegorical figures in relief, has had many examples in England. According to Bolton[16], the greatest artist in this work was Flaxman, many of whose subjects were afterwards translated into pottery by Wedgwood for his jasper ware. Flaxman also made many portraits which were put to the same use.

In the third class, portraits, the earliest English portrait known is a beautiful one of King James I, which was done by Abdonio Allesandro, the younger, an Italian who lived between 1550 and 1650. Another sixteenth century wax portrait modeler was Leone Leoni, who left us a portrait bust of his friend, Michelangelo. In France there are a number of wax portraits (by the artists Clouet, Dupré, and Benoits) preserved in the Cluny Museum. Patience Wright was the first American to model portrait heads in wax. She started on this type of artistic work at Bordentown, New Jersey, in 1769, but moved to London in 1772, where she was acclaimed as the most skilled in the art by Horace Walpole. She made many models in life size of English notables; her full-length portrait of Lord Chatam found a place in Westminster Abbey after his death. Her models were also made in the round. Her relief of George Washington in white wax is the best example of her work in America. Her son, Joseph Wright, returned to America and modeled in wax the designs for the first coins minted in the United States.

Waxes are so frail, and so subject to the action of heat and cold, that not many of the earlier objects of art have come down to us intact. The artists always worked with their secret formulas, which were not only in white but in all sorts of colors. Vasari, the chronicler of Italian painters, writes of the medieval method of preparing wax for use: "To render softer, a little animal fat and turpentine and black pitch are put into the wax, and of these ingredients it is the fat that makes it more supple, the turpentine adds tenacity, and the pitch gives it a black color and consistency, so that

after it has been worked and left to stand it will become hard." Many portraits were done, as Flaxman's allegorical figures were, in white wax. In the Lewis Harcourt collection in England there is a beautifully modeled portrait of William Pitt in pink, done by Peter Rouw, the best of the English artists. Wax portrait modeling also flourished in the Victorian era. The Essex Institute at Salem, Massachusetts, has examples of early wax portraits. One of these done by Rauschner, a Dane, is of a family group, mounted as usual on glass painted a slight seal brown on the outer surface. The wax of his portraits is colored all the way through, according to medieval recipe, and only the small parts, like the eyes, eyebrows, and slight shadows, are painted in. Some sculptors modeled their portraits on velvet, either in color or in white wax. Fine qualities of white lead were mixed with wax to produce opaque whiteness, but the compositions turned yellow in the course of time from sulfur gases. Hughes, an English sculptor, came to America and modeled reliefs in wax that would remain white, but never revealed his formula. With the death of Hughes the art languished in America, although there have been many attempts made to revive it.

Batik or Wax Printing. Batik is a Javanese word for wax printing. Little is known of the origin of the art; it was probably developed during the Hindu immigrations over twelve centuries ago, for some of the stone figures found in the ruins of the ancient temples of Java portray garments similar to those worn today by the natives and decorated with similar patterns. Batik is used almost entirely throughout Indonesia for the decoration of the very simple clothing which the people wear, as well as the beautiful costumes worn by Javanese women on festive occasions. The clothing consists of four pieces—the *sarong*, a strip of cloth 9 to 14 feet long and 3½ feet wide twisted about the body; the *slendang*, a cloth 9 feet long and 18 inches wide, which may be twisted about the head or used to carry burdens on the back; the *kemban*, a narrow girdle or band, worn only on occasion by the women, twisted lightly about their waists or breasts; and the *sarong kapala*, a large bandanna handkerchief, worn by the men, twisted and starched to form a headpiece.

The technique of applying the wax "resist" to the cotton cloth and sometimes silk, and the nature of the design, differs from village to village. Knaggs has described the methods used in the batik centers of Jokjakara and Solo in "Adventures in Man's First Plastic"[100c], to which the reader is referred.

The cloth undergoes a certain amount of elaborate preparation before the design is traced; the fabric is spread over a framework of bamboo poles and stretched tight. Seated on the floor the batik worker places her left hand beneath the cloth in order to support the pattern to be covered with wax. With her right hand she dips the wax-applying instrument, called a

tjanting, into the wax, which is kept molten in an iron vessel on a small clay hearth. The tjanting consists of a little bowl with a small downward-curving pipe attached, through which the wax flows; it has a bamboo handle about 3 inches long which is fastened to the other end. Once the bowl is full of liquid wax, the worker blows through a small bamboo mouthpiece to keep the wax fluid. There are a number of types of tjanting employed, so as to have a range of orifices for various widths of design, and special ones for executing intricate patterns. Painting with hot wax requires a great deal of skill.

The batik worker traces the design in hot wax on the cloth, which is then dipped into a dye, impregnating all areas not protected by the wax. Once the color has set, the wax is scraped off; this permits the design to be dyed with another color. The wax "resist" is usually composed of *beeswax*, *paraffin*, and sometimes a little resin, which makes it adhere more readily to the material. Vegetable dyes are used primarily, the blue being indigo, the red madder, the yellow from a native tree. Secondary colors are formed by the dyeing of one of these colors over another. Some batiks take many months to complete and are considered masterpieces of art, with their beautiful colorful designs.

Modeling Flowers in Wax. "The art of imitating flowers in wax is perhaps the most beautiful method known of preserving a life-like representation of garden-gems, as the form, color, and texture can be imitated to perfection," wrote Worgan[178] in 1867. He records that the wax supplied for such purposes is prepared in sheets, and directs how it should be used. "Should you wish to imitate a thin petal, take the *thin wax*; for a thick one take the *thick wax*; and should you require a still thicker petal, double the wax together."

The wax used in modeling flowers was white beeswax, and the sheets were available not only in natural white color, but also in tints of green, and a shade of light yellow. The colors as a whole were applied from powders of white, chrome yellow, carmine, ultramarine blue, Prussian blue, vermilion, and magenta or solferino pigments, and numerous tints of such colors. The dry color was always rubbed on the modeled wax with the fingers.

Worgan gave directions for fashioning imitation roses: "Cut the larger-sized petals out of *thick* white wax or thin wax doubled—the two smaller sizes from *thin* wax; rub them with sofrano rose bloom, tint some of the petals with light pink powder, also rubbed on, taking care to leave a portion of the petal uncolored at the base, as this is the part you require to join to the foundation." The color referred to was one of a great many supplied by the H. H. Dickinson Pharmacy, of Brooklyn, New York, to artisans of that time.

The industry of modeling flowers in wax is now a highly specialized one

and comprises a large number of operations performed by separate hands. The process consists of cutting up the various fabrics and materials into shapes suitable for forming the leaves, petals, etc. This is done by scissors, or by mechanically operating stamping presses. The veins of the leaves are impressed by means of a die, and the petals are given their natural rounded forms by buffering irons of various shapes. The next step is to assemble the petals and other parts of the flower, which is built up from the center outwards. Then the flower is mounted on a stalk formed of brass or iron wire wrapped with suitably colored material, and leaves are fastened on to complete the spray. In artificial wax flowers the fabric materials are coated with wax. A composition suitable for producing such flowers, according to Fuchs[49], consists of the following: balata 38, gutta-percha 3, wood tar or rosin oil 4, *carnauba wax* 12, *beeswax* 42, copal resin 3, organic coloring matter 3, and *aluminum palmitate* 1, parts. It is also possible to modify the composition by leaving out the gutta-percha and copal resin. The ingredients are melted together at a temperature of about 150°C.

The modeling of plants of wax, as conducted by museums, involves squeeze mold casting, since this gives the exact reproduction of the sprays of leaves and flowers. A full description of the art of making a squeeze mold for museum work is given by Coleman[34], to which the reader is referred. The description of squeeze mold casting given below refers to the art in a more general manner.

Squeeze Mold Casting. In order to reproduce objects one may employ what is known as squeeze molds made of metal, plaster, or thermoplastic, and waxed cloth as a positive to receive the impression. For example, in reproducing sprays of leaves and flowers, the leaf may be placed in a clay bed and the first half of the mold made by pouring liquid plaster upon the leaf. It may be necessary to reinforce the midrib of the leaf by means of a fine wire, so that a similar impression can be made from the reverse side for the second half of the mold. These molds are known as squeeze molds. The mold and counter-mold of plaster may have suitable grooves so as to facilitate matching them up, and be provided with a strap hinge and handles.

In using a squeeze mold it sometimes becomes necessary to soak it in hot water in order to prevent the positive from chilling. The waxes used for the positive are beeswax and fully refined paraffin; e.g., a blend of *paraffin wax* (143/145°F-AMP) 1, and *yellow beeswax* 7 parts. The positive material, in this instance waxed cloth, is placed between the faces of the leaves, and the wire reinforcement described above is made long enough to form the stem.

Casting a Wax Leaf. The following method is one that has been described by Coleman[34] as used in the production of plants of wax at the American

Museum of Natural History. When leaves are to be cast from a squeeze mold, the mold must be soaked in hot water and used while warm and moist. Heat keeps the wax from chilling until it fills the mold and moisture prevents it from adhering to the plaster. A film of cotton is laid upon one side of the mold—better the concave side if either one is so. A piece of cotton-covered hard iron wire is laid along the line of the midrib, with its end projecting from the stem. Melted wax, tinted green with oil color, is then poured upon the upper part of the mold, and squeezed down upon it. The whole is plunged into cold water, opened, and the cast removed.

According to Coleman, the wax should be bleached beeswax to which is added about a tablespoonful of Canada balsam to each quart of melted wax, the object of the balsam being to toughen the wax. Wax should be melted in a double boiler. The oil color is thinned with a very little turpentine, and thoroughly stirred into the melted wax; this gives the body color of the leaf to be imitated. Foliage for imitation may be preserved by the following composition: formalin 15, water 35, and glycerin 50 parts.

After removing a cast from a mold, the mold is set aside to dry and before it is used for another casting it should be hardened by boiling in a strong solution of borax for about 20 minutes or soaking in melted paraffin for about the same time.

Dental Waxes. Manufacturers of dental supplies furnish dentists and dental laboratories with many kinds of wax compositions, such as *base-plate wax*, *inlay-casting wax*, *sticky wax*, *carding wax*, *bite wax*, and *carving wax*. The waxes used for compounding by the manufacturer comprise paraffin of both lower and higher melting points, carnauba, candelilla, shellac, ozocerite, petroleum ceresin, beeswax, and synthetic waxes such as "Acra Wax C," "Aerosol OT," and "Castorwax." Stearic acid is also used. Damar resin is used in the formulation of base-plate wax; and those synthetic resins of a nontoxic character which will combine with waxes are used in some dental compositions.

Base-plate Wax. Base-plate wax is a composition used in taking impressions of the mouth-gums preparatory to making the dental investment of plaster of Paris which precedes the making of the denture with artificial teeth. For base-plate wax the resin and beeswax must not only be light but standardized in color. In the compounding, the resin is preferably melted in a stainless steel kettle, and the waxes added and carefully blended by stirring. The molten mixture is filtered through several layers of cheesecloth, or a fine-mesh metal screen, and then the rhodamine or other suitable color, previously dissolved in part of the paraffin, added to obtain the desired flesh gum shade. The mixture is again filtered and poured into flat tin pans where the wax composition is congealed and remains until ready for use. The cakes are removed from the pans and heated in warm, slightly acidified

water, and milled on a two-roll mill, with rolls operating at the same speed to produce a perfectly smooth polished sheet of wax composition. The best rolls appear to be those made of highly polished granite, which are capable of rolling the wax in a continuous flat strip of 0.070 inch thickness or less, as required. The strips are customarily stamped before packaging.

Inlay Casting Wax. The first step in the actual construction of a cast restoration is the preparation of a pattern usually constructed of wax. In practice, the wax is softened by heat and then forced into the cavity preparation under pressure where it is held rigid. It is then burnished and carved to the anatomy of the tooth, obtaining as near as possible an exact reproduction of the finished restoration. It is obvious that an *inlay-casting wax* must be one which has been compounded with considerable care to conform to the exacting requirements. Inlay-casting wax is prepared from paraffin or petroleum ceresin wax and a large proportion of high-melting hard waxes, such as carnauba, carnauba replacement, "*A-C Polyethylene*," and/or nontoxic resin. Secrecy surrounds the exact composition of such waxes sold to the dental profession. However, the principle of their compounding is given in Coleman's inlay wax: carnauba 25, paraffin 60, ceresin 10, and beeswax 5 parts, to which a suitable coloring matter is added. This inlay wax becomes soft and plastic at 45–50°C (113–122°F), and is completely eliminated from a casting mold at 250°C (480°F). Most commercial inlay waxes, according to Skinner[153], start to smoke at 115 to 143°C and flash at 83 degrees higher.

Skinner[153] has added certain requirements to the specifications of the American Dental Association Research Associates at the National Bureau of Standards, which are given in specification Nos. 7 and 8, in the abridged standard as set forth below:

(1) The waxes should soften without becoming flaky or laminated.

(2) They should be sufficiently plastic at a temperature slightly above mouth temperature to permit forcing them into all the details of the cavity walls.

(3) They should harden sufficiently at mouth temperature to permit withdrawal of the casting.

(4) They should curve without flaking.

(5) The color should be in contrast to that of the mouth tissues.

(6) The thermal expansion characteristics should be known.

(7) The waxes should be cohesive, but not adhesive.

(8) They should vaporize at a temperature compatible with normal casting practice without leaving residue other than carbon.

Sticky Wax and Other Waxes. Sticky wax is sticky as the name implies and is used in dental laboratories for the preparations on investments, such as making ridges, and for general laboratory technique. Sticky wax is

prepared from beeswax, ceresin, or a microcrystalline petroleum wax, "Aerosol," and Venice turpentine, and cast into sticks. *Carving wax* is a wax that is prepared hard so that it may be carved in the mouth in making gold inlays. It is harder than the regular inlay-casting wax and is used particularly in making gold inlays, and as a means of taking well-defined impressions in dental laboratory technique. Carving wax must be noncrystalline, of high fusion point, cohesive, and hard, though free from brittleness. It is made from a mixture of high-melting waxes including carnauba. *Carding wax* consists mainly of a high-penetration petroleum wax, and is extruded in suitable ribbon shape for mounting artificial teeth. *Bite wax* is a wax that must have a high plasticity at normal temperature, and yet have cohesive instead of adhesive properties. Beeswax is used for the purpose, also beeswax and petroleum ceresin 170/180°F ASTM. *Temporary filling compounds* are made of gutta-percha with less than 1 per cent of wax.

WAX APPLICATIONS TO PAPER PRODUCTS AND FOILS

It has been estimated by the Waxed Paper Institute, Chicago, Illinois, that it takes 350,000 tons of waxed paper each year to wrap America's bread, cereals, pastries, frozen foods, cheeses, meats, fruits, candy, tobacco, drugs, and many other essentials. The largest use of wax, particularly petroleum waxes, is in impregnating and/or coating cellulosic material. The consumption of vegetable waxes alone is only exceeded by the polish industry. The greater part of the wax consumption by the "paper converters" is for the ultimate purpose of paper packaging. Because of its excellent protective qualities, its self-sealing factor, its ability to withstand a range of climatic changes, and its ready adjustment to factors of size, shape, and weight, the uses of waxed paper in protective packaging are almost limitless.

There are many ways in which wax is applied to paper material, and these methods will be referred to later. Wax is used for waterproofing paperboard as well as sheet paper. The paper converters use continuous line production machines which wax and slit the paper to the required widths. Squaring sheets to specified size is an operation in addition to slitting. A wrapping material is printed from a roll of paper slit to the required width, by means of a rotary electrotype which is inked, and then the printed paper is paraffined or otherwise coated with wax.

Papers that can be waxed include greaseproof krafts and manilas, tissues, twisting papers of several grades, regular or opaque sulfites, and glassines. Waxed paper can be made opaque or highly transparent depending on needs, method, and stocks. No other single coating material combines the properties of moisture protection, flexibility, heat sealing, high finish, low

cost, and efficiency so well as wax of the right quality applied to the right type of paper.

The whole process of printing and waxing bread wrappers is automatic. The waxed paper is slit transversely to the required length for wrapping the bread loaves. Household waxed paper generally used for wrapping articles of food is sold in small rolls of 125-foot length. Drinking cups made of paper are waxed, as are paper milk bottles. Paper mills use wax emulsions for sizing special kinds of paper. The lithographed pages of leading magazine publications are customarily sprayed with an infinitesimal amount of wax to prevent them from sticking to each other. Wax is the principal constituent of the coating on heat-sealing foils.

Carbon papers which are used in copying from pencil, pen, and typewriter are manufactured with a "color wax foundation." Many of the waxes used in the arts described above are blends of petroleum hydrocarbon wax with vegetable wax, and occasionally with resin, or rubber. A modern use for wax is as an adhesive in laminating paper material. Playing cards are made glossy by the application of a lacquer composed of nitrocellulose, ethyl cellulose, carnauba wax, and suitable solvents. The glossy surface can be rendered a "mat finish" by treating with a hard wax, such as carnauba, candelilla, or montan wax.

The amount of paraffin wax consumed annually in the United States for waxed bread wrappers alone exceeds 100,000,000 pounds, topped only by the amount of wax used in carton overwraps and paper milk containers. Waxed paper sold in the food stores in the United States in 1950 amounted to $36,324,000. The estimated U. S. consumption of petroleum waxes by the paper products industry as a whole was 760,000,000 pounds in 1951.

Methods of Application of Wax to Paper. A surface-waxed paper is known as "wet-waxed" paper, while one in which the wax has been driven into the paper is known as "dry-waxed." The porosity of the paper or paperboard and the temperature at the time of application largely determine whether the surface will be coated or whether the wax will be absorbed into the paper. The amount of wax applied in coating varies from as low as 1.5 lb per side per ream (3000 sq ft) on glassine paper to as high as 50 lb or 6 lb per ream on paperboard. Wax is also used in the paper industry other than for exterior coatings. The various ways in which wax is used in accordance with the specific needs are the following:

(1) As an emulsion in the beaters at the paper mill. This method has definite limitations.

(2) As a spray on paper material, in which the wax snow spreads well if the paper is warmed, or has just come off a printing press. The spraying is usually done by a Grammer spray machine or the like.

(3) As a coating to paper or paperboard, applied on one or both sides by

rolls. The roll may be smooth, grooved, or wire wound. In a sheet waxer the paper passes between two rolls, of which the lower dips into the coating while the upper has coating supplied to it by a pump. As the paper passes between the rolls, the excess coating is squeezed off.

(4) A paperboard material is impregnated in a bath of paraffin wax, and then directly dipped in a finishing-coat bath of a special wax held at a lower temperature.

(5) The article of paper material may be finished with molten wax by a flushing-type machine.

(6) Immersion of the entire sheet of paper or paperboard in a wax bath. This is common practice. A sealed, filled carton is given a single dip in a waxed bath.

(7) Paperboard material for carton or other use may be sprayed with wax by means of steam-heated wax spray guns.

(8) Cartons sealed at one end may be dipped in wax, or spray waxed, then oven-dried to spread the wax, and finally heat-sealed. This is known as the Dacca method.

(9) Lamination of paper material to similar paper stock or to cellulose or noncellulosic films by using a microcrystalline petroleum wax of a selected sticky grade.

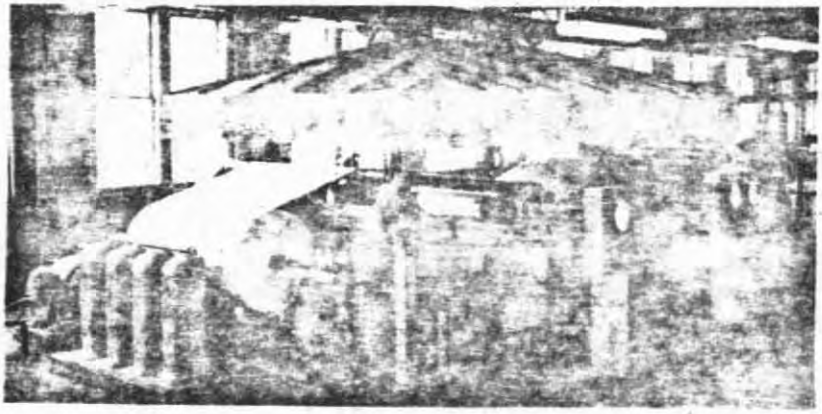
A type of laminated paper that has come into extensive use for refrigerator locker packages is known as "locker paper" and consists of a sandwich of two sheets of glassine with a *petrolatum wax* in between. Wax-laminated glassine of 57 lb per ream is usually made from two sheets of glassine 25 lb per ream each with a laminant of 7 lb of wax. Locker paper has a very low water vapor transmission rate (WVTR) value, which does not change appreciably when the paper is creased in the wrapping of foods, for the freezer lockers.

Protective Paper Packaging. There is a constantly growing demand for paper material which is water-repellent and moistureproof, particularly by those who are engaged in the paper packaging of commodities. Paper may be made water-repellent by filling up the minute spacings between the fibers with wax. This may be done in the industry by dry-waxing, for example, by passing the paper over a wax roll under pressure and then over a heated roll to smooth the very thin film of wax. But to make the paper substantially moistureproof it is necessary to resort to wet-waxing, in which case the application of the wax is in a continuous film, with only enough wax impregnated in the paper to provide a bond for the coating. A third method of imparting both waterproofness and resistance to water vapor penetration is to use two sheets of paper with a layer of wax in between. When metal foils were not available during World War II wrappers for cigarettes were made from a laminated paper in which two sheets of soft

paper were bonded with a black microcrystalline petroleum wax ("Black Wax") between them in a thin continuous film. The resultant wrapper had a water vapor transmission rate comparable with the metal foils. This same principle of lamination has been applied to other types of wrapping material, where exterior watertightness is not required.

Self-Seal Wax Paper. Self-sealing wax paper is used for packaging such foods as breads, biscuits, cake, candy, and meat. It has special advantages for use in packaging baked goods, because it offers an ideal method for consumer resealing of unused portions of food. It requires no special sealing equipment, that is it can be used on a number of automatic packaging machines employed for other wrappings. Self-sealing wax paper can be heat-sealed on both sides, as well as sealed by surface pressure with special adhesive which adheres only to itself. Advantages of the paper are in its imperviousness to the passage of air, odors, and moisture.

Bread Wrappers. "Bread wrappers" is a term applied to sheets of light-weight wrapping (usually sulfite paper) almost always waxed and in two styles: (a) self-sealing and (b) so-called "dry" waxed. In the case of paper of class (a), the major portion of the wax lies on both surfaces of the sheet, so that when two sheets are pressed together, and heated the surface wax melts, causing the sheets to become sealed together. Heat seals are normally made by passing the wrapped packages automatically between heated plates and then between refrigerated plates, with the application of pressure during both the heating and cooling stages.



Courtesy Dilts Machine Works Division
The Black-Clawson Company, Inc., Fulton, N. Y.

FIGURE 33. High speed waxing machine suitable for producing bread wrappers, household waxed papers, drinking cup stock, delicatessen waxed papers, etc. Machine will produce dry waxed papers at speeds >1700 fpm, or wet-waxed papers at speeds of >1000 fpm.

Papers of class (b) are so waxed that the major portion of the wax is driven into the interior of the sheet and the paper feels dry. This class of wrapper must be sealed by adding melted wax, as the wrapping is being done. Practically all bread wrappers are printed before they are waxed.

The sealing ability of the wax used is an important function in high-speed automatic sealing. Several factors are involved in the selection of the best types of waxes for waxing the wrappers, such as tensile strength, melting point, and congealing point, and sealing strength. *Fully refined paraffin wax* of 132/134°F (ASTM) or higher melting point may be used, or a fully refined paraffin to which has been added about 1 per cent or more of a *polyethylene wax*, preferably of the lower molecular weight. The paraffin wax will constitute 25 to 30 per cent of the weight of the finished self-sealing wrap.

The sealing ability of the wax used is tested in the laboratory by sealing the waxed sides of the paper together between hot glass plates and measuring the force required to separate the heat-sealed papers. Papers such as (a) 25.5 lb per ream sulfite or (b) 24 lb per ream glassine coated may be used in these tests.* The sealing strength is recorded in grams per inch. The corrected sealing strength (S) is computed from the equation $S = A/a \times B$, where A = standard sealing strength value of standard wax, a = measured sealing strength of standard wax, and B = measured sealing strength of test sample. Refined paraffin wax of 147°F (ASTM) melting point with a sealing strength of 2.6 grams per inch (average of 60 determinations) was used as a comparate. It was found that 200°F is required to drain the excess wax, and at this temperature about 7 minutes are required for the wax in the papers to reach a constant level. Factors involved in sealing strength are oven temperature, oven time, and amount of wax on paper for any given wax. Near 10 lb of paraffin wax per ream the sealing strength remains fairly constant at 26 grams per inch. Higher sealing strengths can be gotten by the use of more wax in lb per basis weight of paper. Sealing strength also increases somewhat with sealing temperature.

One formula for a bread wrap wax calls for pale yellow micro wax [150°F (AMP) penetration 25–35] 40, and paraffine [133/135°F (AMP)] 60 parts. Another formula calls for the addition of 5 parts of microcrystalline wax [180°F (AMP)] to the paraffine.

Waxed Glassine Papers. Glassine is a smooth, dense, transparent, or semitransparent paper made customarily from sulfite chemical pulp which has been severely beaten mechanically to secure a high degree of hydration of the pulp to make it more or less gelatinous, and greaseproof. The water

* For details of the construction and calibration of a "sealing strength tester" consult article entitled "Testing wax-seal strength" by C. S. Funk and Associates, *Modern Packaging*, 13, No. 6, 127–129, 182–183 (1950).

tends to drain from such a pulp very slowly necessitating the use of long Fourdrinier wires and a slow speed of the paper machine. Next it is passed over steam-heated driers, wound up on a reel, but then must go through a densification step to make it glassine. The greaseproof paper is dampened and supercalendered at a high temperature (250–300°F) and pressure (up to 2000 lb) by slippage between paper and driven steel rolls, to produce sheen and gloss of the sheet, and increase its transparency and waterproofness. The grade and quality are controlled by the degree of supercalendering; a highly supercalendered paper is more transparent but not as strong. Bag papers are made of the stronger types of glassine, while cake and tobacco wraps are made of the more transparent grades.

Opaque glassine called "dead white glassine," can be made by incorporating titanium oxide pigment in the beater stock. It has a high light reflective index, protecting food products from ultraviolet rays when so packaged. Colored glassines such as green also have a high reflective index. Glassine is produced in colors for various purposes—the colors are called champagne, canary, goldenrod, yellow, tangerine, and oxblood. Glassines are customarily produced in weights of 8 to 30 lb per ream (500 sheets 24 in. x 36 in., or area of 3000 sq ft). This is equivalent to the German standard of 4.92 to 18.45 grams per square meter. Glassines of 20 to 25 lb per ream basis weight are the more commonly used.

The term "converted glassine" is given to glassine which has been waxed, solvent or plastic resin coated, or laminated. These treatments are given to the glassine to enhance water-vapor resistance, heat sealability, chemical inertness, or other desirable characteristics. Solvent coated or wax laminated glassines are usually produced by the glassine manufacturer, whereas waxed glassines, bleached or unbleached, are plain glassines which have been waxed by a converter or often by the user on his own premises.

According to Borden, Jr. and Wolper[16a] the waxed papers are prepared by using plain paraffin wax, modified paraffin wax, or "hot melts." Paraffin wax may be modified with microcrystalline waxes, compatible resins, "A-C Polyethylene Wax," or rubber derivatives and the like. Hot melts are blends with only a small proportion of wax and generally lower the moistureproofness and increase the brittleness of the glassine.

Wax-laminated glassines are prepared by using microcrystalline wax, modified microcrystalline wax, or a dispersion of glue or resin as the laminating agent. The laminated papers may consist of glassine to glassine, glassine to paper or board, glassine to a synthetic film, or glassine to metal foil. These combinations can be attractively printed.

Wax-laminated glassines designated as 57 and 62 lb, or 25/7/25 and 25/12/25 respectively, are made from two sheets of glassine (bleached or unbleached) of 25 lb per ream with 7 lb and 12 lb of wax, respectively, be-

tween the layers of glassine. A 52-lb wax laminated amber glassine is two sheets of amber glassine of 20 lb per ream basis weight laminated together with 12 lb of wax, and carries the designation 20/12/20. A light weight wrap may run as low as 47 lb per ream, or 20/7/20. A heat sealing white bag glassine is made in which the wax-laminated glassine is coated with lacquer on the outside, giving it excellent moistureproofness and splendid heat-sealing properties.

Refined paraffin wax provides both a cheap and excellent moistureproofing film for glassine. Waxed glassine is used in wrapping cakes and potato chips, and is also used in cereal boxes and cracker boxes[16a]. For the latter purposes it is customary to wax unbleached glassine of 25 lb per ream weight with about 7 lb of either paraffin or modified paraffin wax. Paraffin wax may be modified with *microcrystalline wax, ozokerite wax, "A-C Polyethylene Wax,"* compatible resins, or rubber derivatives. The formulations of modified blends are designed so as to improve heat-sealing and blocking characteristics, thus permitting the waxed glassine to function well in automatic packaging. "Hot melt" coatings are seldom applied to glassine since they cause it to become brittle and less waterproof.

A glassine of high or medium transparency of 20 to 30 lb base weight when coated with 3 to 4 lb of 100 per cent paraffin wax will have a water vapor transmission rate (WVTR in g/100 sq in./24 hr) of 0.2 to 0.4 flat and 3 to 5 creased. The waxed glassine has a high gloss, good transparency, and is good in greaseproofness. It is poor in heat sealing. A low transparency glassine of 25 lb basis weight and coated with 5 to 7 lb or refined paraffin wax will have a WVTR value of 0.1 to 0.2 flat and 2.5 to 3.5 creased. It has a fair greaseproofness, a high gloss, but only fair transparency. A 32-lb vegetable parchment coated with 8 lb of wax per ream has a WVTR value of 0.4 to 0.6 flat, good greaseproofness, and good wet strength.

Glassine to glassine sheet materials have so low a WVTR value that it is desirable to express the moisture vapor transmission rate as MVR or moisture vapor resistance, where MVR is the reciprocal of WVTR, or $\frac{1}{\text{WVTR}}$. For example, wax laminated glassines at 95 per cent relative humidity (RH) and 25°C gave WVTR values of the following order: 47 lb per ream (20/7/20) 0.274; 57 lb per ream (25/7/25) 0.246; and 62 lb per ream (25/12/25) 0.1244. The corresponding MVR values would be 3.65, 4.06, and 8.04. Glassine to glassine sheet material where microcrystalline wax was used as a laminant showed MVR values ranging from 3.33 to 14.3 and held these values quite well for the creased material.

Laminated glassines are used as a bag liner for whole bean coffee; as a wrapper and carton overwrap for chewing gum; as a carton liner for powdered milk and prepared mixes (cake and pie, or pudding); as heat-seal

envelopes for dehydrated foods, and for certain metal goods; and as an "inaseal" cap liner for medicinals and instant coffee. The glassine may be laminated to kraft for fruit bags, or as an overwrap for meat or fish. Coated laminated foil glassines are used for heat seal envelopes for instant coffee or instant fruit beverages, and dehydrated foods. Some of the uses of waxed (not laminated) glassines are as an overwrap for cupcakes, crackers, cookies, and pastries; as a carton liner for cereals; as glue-seal bags for popcorn, or heat-seal bags for potato chips; as wrappers for metal goods; and as inner wrappers for hard milled soaps.

Packaging of Frozen Foods. Waxed parchment and waxed paperboard boxes are widely used in the packaging of frozen foods, as the frozen food processors have been quick to see the advantage of a wax coating. Waxed parchment is used for wrapping fruits and vegetables, and the wraps are heat sealed and placed in waxed paper cartons. Berries and sliced fruits for freezing are usually packed with sugar or heavy syrup and hence require liquid-tight containers. Heavily waxed cylindrical or cup-shaped cartonettes are used for the purpose, as they are easily filled and leakproof. Empty cup-shaped cartonettes meet with favor with the processor since they nest well, although neither the cup-shaped nor cylindrical cartonettes are as economical of freezer space as cubical ones. The latter, heavily waxed and heat-sealing, are easily filled and may be compactly packed in the freezer.

A popular type of package for fruits and vegetables is the folding rectangular carton, heavily waxed. A shallow form of this carton, lined on the inside with a sheet of moistureproof cellophane, or specially coated vegetable parchment, is used for packaging all kinds of vegetables, including corn-on-the-cob and asparagus tips. In 1941 the Western Research Laboratory, U. S. Department of Agriculture, Albany, California[137] undertook many experiments in the dip-coating of frozen commodities per se, such as frozen poultry and meat, or of packages containing frozen foods, in which modified soft microcrystalline paraffins were employed. This art in packaging came into commercial use in 1946. For example, loose frozen peas have been compressed and dip coated, and frozen peas packaged in a dip-coated bag or in a dip-coated paperboard box. Rabak[137] reported that peas packed in paperboard packages and stored for 20 months at −15°C lose about twice as much weight as if stored at 0°C. The weight loss should be definitely less than 5 per cent if the color, flavor, and physical characteristics are not to be impaired. It is customary to evaluate containers by storing the filled container in air at −15°C and 85 per cent relative humidity for 2 and 4 months. A test control is a container which has been stored at 20°C and 65 per cent RH for 24 hours, with the same commodity. The deformation of a container filled with water at −12°C and subsequently thawed out at

20°C and 65 per cent RH is computed from measurement of the cross-sectional changes. An 800-ml container should not bulge more than about 10 per cent by this test. With thawing foodstuffs a correlation appears between the container stiffness and the permissible deformation. Water-vapor and air-resistant thermoplastic material which will remain flexible and tough at low temperatures is required as a dip-coating. The microcrystalline waxes are tacky, but at temperatures below 0°C they become tough and firm. As pointed out by Rabak[137] undue tackiness is also easily prevented by spraying the dip-coated item under controlled conditions with a thin coating of clear lacquer, which also serves to enhance the finish and appearance. Furthermore, such hydrocarbon coatings may be made more attractive by coloring the melt with oil-soluble permitted food dyes.

Tressler[161] states that when the paperboard boxes are filled, they should be overwrapped and heat-sealed in either moistureproof cellophane or specially coated vegetable parchment. Ground meats may be packaged in heavily waxed paperboard cartons, or waxed folding cartons, adequately moisture-vapor-proof lined on the inside. Meat are suitably wrapped and packaged in waxed rectangular folding cartons lined with moistureproof cellophane or parchment.

Production of frozen foods in 1944 approximated 600,000,000 pounds, compared with 450,000,000 pounds in 1943.

Wrappers for Cereals. Prepared breakfast cereals, crackers, and biscuits, most of which are in paper and film packages, are often given added protection for Southern areas by the use of an outer moistureproof wrap. All Kellogg cereals are packaged with an outer waxed wrap for distribution in Texas, Alabama, Louisiana, Georgia, Florida, parts of the Carolinas, and Virginia. This outer wrap, in combination with an inner waxed bag, has been used by Kellogg for thirty years, giving practically double protection. [Anon., *Modern Packaging*, **24**, No. 10, 75 (1951)].

An inner wrap or bag for a breakfast cereal package is usually one of wax unbleached glassine. The glassine is normally of 25 lb per ream basis weight coated with 7 lb per ream of paraffin wax of 138–140°F (AMP) grade. The 32 lb per ream waxed glassine has a water vapor transmission rate (WVTR) of 0.0755 gram loss/100 sq in./24 hr when flat and a WVTR value of 0.8100 when creased.

Butter Cartons. Butter and oleomargarine are customarily packaged in fold-in cartons after the stick or print has been wrapped in "butter paper," which is a greaseproof parchment or waxed tissue. The cartons are made of white patent-coated solid manila or of solid manila and single manila-lined chipboard; usually waxed or paraffined. Butter cartons are also made by the paper converter from a sheet of heavy virgin sulfate, wound in rolls with the grain running the length of the sheet. The rolls

are shipped from the paper mill to the carton manufacturer. The sheet material is 0.012–0.014 inch thick before printing and waxing, and 0.0128–0.0149 inch thick after waxing.

The paper is printed or lithographed, dried out and embossed with fold marks, and waxed by immersion in a wax bath held at a temperature of about 200°F followed by water chill at 40°F. The wax used for this purpose should have a softening point of not less than 130°F, and a melting point of about 145°F. The penetration value of the wax should range between 8 and 10, and the durometer hardness approximate 75. A paraffin wax of 134–136°F melting point with the addition of a few per cent of a suitable polyethylene concentrate is suitable for the purpose. The desired properties of the wax are a good flowing property to avoid producing a pebbled wax surface, a high degree of hardness combined with good tensile strength, good antiblocking characteristics, and freedom from both taste and odor. About 5 pounds of wax are used per 1000 cartons. The waxed carton is shipped by the paper convertor in the flat form and is folded and locked when the butter is packaged.

In butter packing, bulk butter is unloaded from large cartons and the 64-pound cube is placed on hydraulic pre-cutters from which they are fed by stainless steel elevators directly to the packaging lines. Here the butter chunks are compressed into an adjustable mold, which insures accurate weight. Parchment paper is fed from a continuous roll located about the machine, to wrap a stick or print as it is formed. In one method the overwrapping is done with a waxed sheet of cardboard thickness, and the wrap passes through three electric plates to seal the ends and back seal before entering the compression belts. The operator removes the package at the heat sealer to check the weight.

Wax in Paper Sizings. Materials commonly used by the paper manufacturers in sizing papers include rosin, various hydrocarbon and natural waxes, starches, sodium silicate, glues, casein, synthetic resins, and rubber latex. Writing and wrapping paper are typical sized sheets. Rosin when used as a size is presaponified in part with alkali; and sodium aluminate (alum) may also be used to precipitate the rosin size on the fibers as very small particles.

Paraffin is the hydrocarbon wax most commonly used in waxed sizes. It is not saponifiable and must be prepared for use by emulsifying it in water, thus obtaining a water dispersion of wax particles surrounded by a protective film which keeps them from agglomerating into a solid mass. *Microcrystalline wax* is also used in producing size paper; the wax chosen is one having a high penetration value and having a melting point of about 160–165°F. There are numerous emulsifying or assisting agents from which a suitable one is selected. *Montan wax* acts as a stabilizer of emulsions when added to paraffin. Where the hydrocarbon wax is used as a "size"

and as a "beater additive" the paper necessarily contains very little of it, since after all most of the sizing materials that go into the beater are run to the sewer; only those adhering to the fibers find their way into the formed sheet. Hence, paper sized with either paraffin or microcrystalline wax has little of the feel of either a wax-impregnated or wax-coated paper, but nevertheless tends to be much less resistant to penetration by liquids than unsized paper.

Sizing with rosin has varied completely saponified rosin to a mixture of about ½ rosin soap and ½ free rosin carried thereby as an emulsion. So-called rosin emulsions are really suspensions of finely divided rosin. Mixing *paraffine*, *microcrystalline wax*, or *ceresin* with a rosin emulsion, and later using alum and a pH of 4.9, affords a 50 per cent saving in rosin. Bennett[15] gives a recipe of a paper sizing which is as follows: rosin 70, soda ash 7, *beeswax* 2, and water 21 parts. The ingredients are boiled together until a sample solidifies on cooling. This material may be shipped solid to be dispersed in hot water when needed.

The amount of sizing is dependent upon the kind of furnish used in the papermaking. Book paper has 0–2 per cent, writing paper 2–3 per cent, kraft 1½–2½ per cent, wrapping 2½–3½ per cent, wall board 2–5 per cent, and container board 3–5 per cent size. The ratio of wax to rosin in sizing is commonly about 1½ rosin to ½ wax. The techniques of sizing are many and varied. The agent may be a beater additive to give "stock" or "engine" sizing, or the sheet run through a size solution or on a roll wetted with size solution to give sheets which are termed "tub-sized" or "surface-sized."

Wax in Greaseproof Paper. Paper is greaseproofed by (1) treating at least one surface with a material which contains no wax, (2) sizing the surface with a nonwax material and then waxing the sized paper, or (3) treating the paper directly with a wax composition. An example of (1) would be the treatment of paper with a solution of rubber hydrochloride; of (2) the priming of a paper sheet with bentonite and cooked starch, the filming of the treated surface with zein, and finishing with about 2 to 4 pounds of wax to 2880 square feet, as in the process of Schur[147]; and an example of (3), the dipping of the sheet in a wax mixture and passing it over a heated roll, then a chill roll.

The number of formulations published for greaseproofing is tremendous. A typical one is that of Cable[24] who states that a paper can be made greaseproof by dipping it in a wax mixture heated to over 56°C and passing it over rolls heated to the same temperature followed by chilling with rolls kept at a temperature of 4°C. The wax mixture comprises *anhydrous lanolin* 6, *paraffin wax* 2, white petroleum jelly 2, and white spirits 4 (or less) parts by weight. To mask the odor 1/16 part of eucalpytus oil is used.

Sulfite-lined chipboard used for trays and boxes of the fold-in type hold-

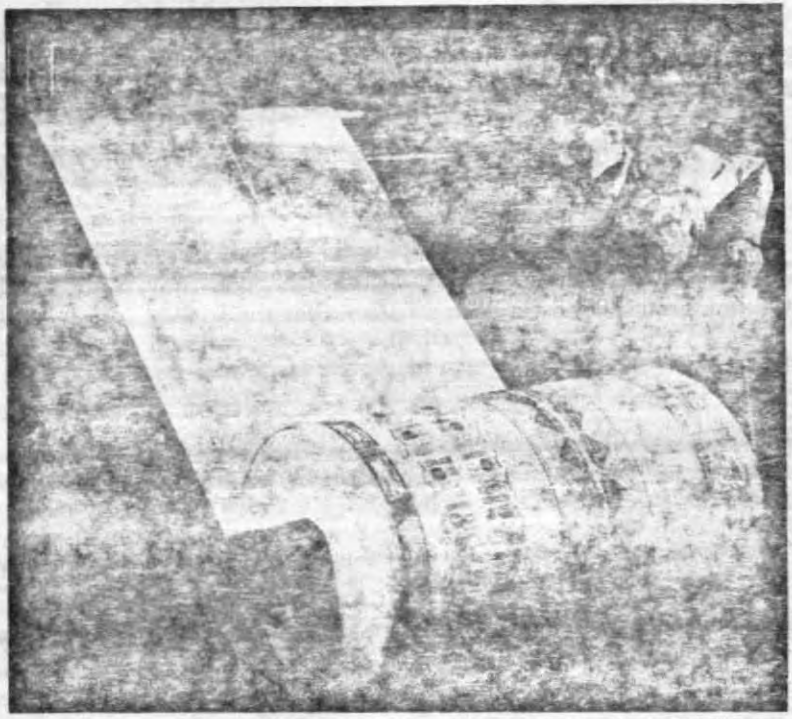
ing cakes containing shortening, or other greasy food items, may be waxed on the inside (gray side) with paraffine containing a substantial amount of polyethylene wax, which latter provides a good greaseproofing agent for flat paper surfaces.

Waxed Paper Wrap Material. A waxed paper, translucent and pliable, is made for automatic wrapping and sealing machines, by supercalendering a nongreaseproof paper sheet with molten *petrolatum* of high melting point, prior to the final waxing operation. The automatic wrapping machines usually fold portions of the waxed paper on itself and seal the fold around the wrapped article by melting the wax on the sheet.

Briefly the process of waxing, according to Dodge[48], is as follows: The paper to be treated is in the form of a mill roll, and is guided by means of two rollers into contact with the surface of a fountain roll, the lower portion of which is immersed in a bath of melted petrolatum. The petrolatum is contained within a tank provided with heating elements, such as steam pipes, for maintaining the petrolatum at 150–175°F. As the fountain roll revolves, it picks up a film of molten petrolatum, the excess of which is doctored off by means of a roll or rod doctor. The film of petrolatum remaining on the fountain roll is transferred to the underside of the paper. The paper sheet will thus be impregnated with petrolatum, preferably to the extent of 1½–2½ per cent by weight. After leaving the fountain roll the web passes around a steam-heated roll and thence is led by two guide rolls to a rewinder, where it is rewound at the rate of 500 ft per minute. The petrolatum-impregnated paper is then subjected to a waxing operation by passing it through a molten bath of wax in accordance with known practices (see p. 792).

For high quality waxed paper wrap material used in the packaging of fine cakes, etc., it is advantageous to use a petrolatum with a substantial, if not predominant, amount of microcrystalline wax so that the creased or crumbled sheet of waxed paper will not show rupture of the wax coating. It is possible to prepare commercial waxed papers with a water-vapor transmission rate value as low as 0.2 gram per 100 sq in. per 24 hours at a temperature of 100°F, and a relative humidity of 95 per cent on the wet side.

In the modern process of waxing printed and plain paper and cellophane wrappers it is customary to have the wax delivered to the plant in liquid form and to pump it to the waxing machine through pipes electrically heated to maintain the wax at any optimum constant temperature. For example, the wax is delivered in tank cars that are equipped with steam coils to facilitate melting for removal. At the Central Waxed Paper Company, Chicago, Illinois, the wax delivered in tank car lots is stored in five steel insulated tanks, each of 100,000-pound capacity, located in the extreme corner of the site (150,000 sq ft) and surrounded by concrete dikes.



Courtesy Esso Standard Oil Company

FIGURE 34. Waxed wrapping paper, here shown during processing, remains one of the largest uses of fully refined paraffin wax. The roll of waxed printed paper is then slit to wrap widths and rewound in spool form for later use.

Waxes Used in Waxed Paper Art. The wax most commonly used in the waxed paper art is *fully refined paraffin*. The range in melting point is from 127° to 140°F by the English method of determining melting points. In making a waxed paper for bread wrapping it is customary to use a sulfite sheet of 20 to 25 pounds weight to the ream, and wax this up to 33 to 37 pounds per ream. According to Padgett[126] the addition of a small amount of other very high melting wax to the paraffin will improve the tensile strength of the wax and increase the strength of the seal to the package. *Microcrystalline wax* of 190°F melting point, "Castorwax," and polyethylene wax such as "A-C Polyethylene," are of value for the purpose.

"FT Waxes" which are synthetic paraffin waxes made by Krupp Kohlechemie (G.m.b.H.), Wanne-Eickel, Germany, are used in the paper industry where characteristics of high congealing point, extreme hardness, and high gloss are desired. "FT Wax 200" has a melting point (drop) of 105.8°C (222.4°F) and "FT Wax 300" a drop point of 110°C (230°F).

"FT Waxes" may be used in the impregnation of paper cups which are to hold hot liquids, or for paper containers that are to be filled with hot jams or jellies. They are also used with resin polymers in laminating papers for containers that are to be sterilized.

For papers which do not require hermetic sealing but simply a degree of waterproofness, *petrolatum* is commonly used; petrolatum of the highest melting point is preferred. Waxed wrappers for packaging potato chips and other dry food materials that require sealing may be prepared by treating glassine paper with a hot melt of ethyl cellulose, resin, and wax. The coating material must be of such a nature that the treated paper material will have a very low coefficient of water-vapor penetration, will flex under a wide range of temperature, and produce a tight strong seal under application of heat. Rubber-wax blends are also waterproof and produce a lustrous finish to the wax coating.

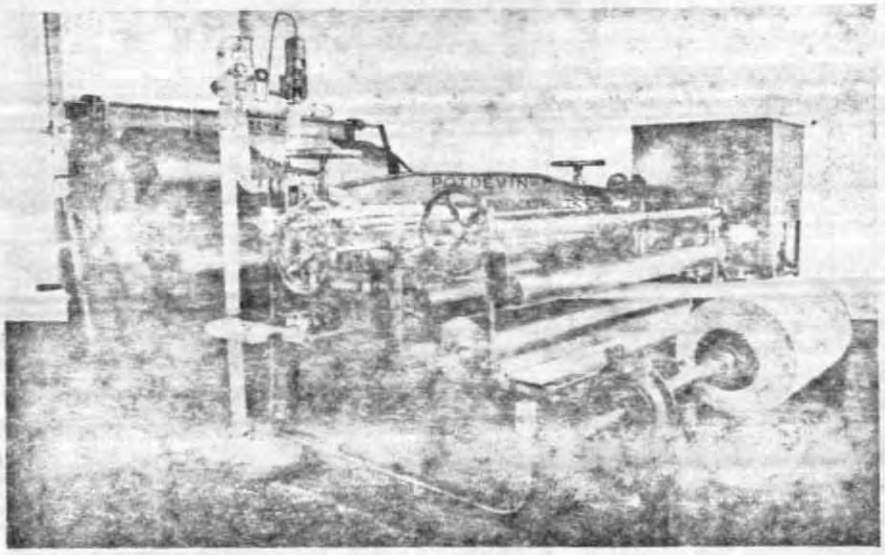
The value of a blend of paraffin wax and microcrystalline wax in preparing coated paper for wrapping foods is set forth in a letters patent of Adams and MacLaren[6]. The mixture is prepared with not more than 10 per cent of microcrystalline wax having a melting point above 63°C (145°F); the latter should be relatively oil free so as to have less than 2 per cent of occlude oil in the mixture. In the prior art, *beeswax*, *japanwax*, *ozocerite*, resin, etc., were added to *paraffin wax* to inhibit the formation of coarse crystals of paraffin when the wax was chilled. A thin film of paraffin, even if continuous, is never more than 50 per cent impermeable because of the interlacing fine needles. The inhibitor greatly increases the impermeability.

MacLaren states that an opaque composition suitable for coating paper, etc., is formed of *paraffine* with an admixture of 0.5–5 per cent of a hydrogenated vegetable oil such as *hydrogenated cottonseed oil*. (MacLaren, F. H., U. S. Patent 2,159,218 (1939).

Waxing Paper and Pasteboard. The terms "dry waxing" and "wet waxing" are frequently used in the paper and paperboard industries to denote not only the method of application of the wax to the paper material, but also the character of the waxed surface. For many purposes it is desirable to apply an exceedingly thin film on the surface of the paper material and hence dry waxing is resorted to. Examples are builder's papers, chewing gum wrappers, fish paper, florists' paper, fruit wrappers, labels, etc. The addition of a very small amount of a high melting microcrystalline wax of the harder kind or of polyethylene wax will prevent waxed tissues from blocking.

In the waterproofing of pasteboard material the pasteboard is passed through a bath of *paraffine*. The addition of a little *aluminum palmitate* to the paraffine will keep the pasteboard from darkening.

The waxing of paper may be carried out on a rather simple machine, as



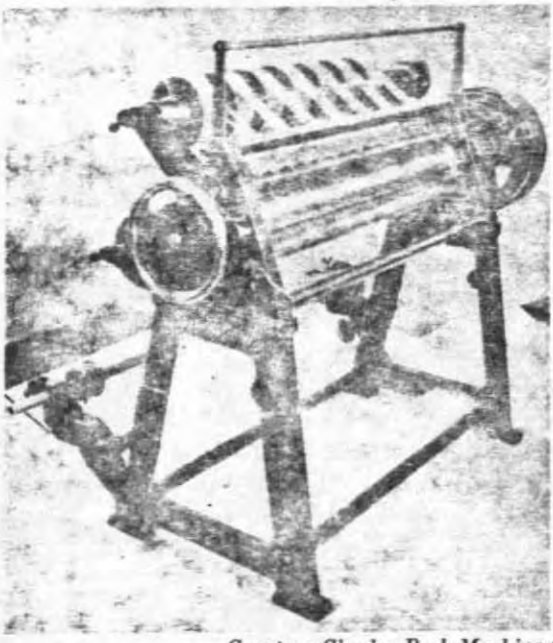
Courtesy Potdevin Machine Co., Brooklyn, N. Y.

FIGURE 35. Typical plant installation for general utility use in waxing paper. The machine has steam and water connections—steam for wax pan and auxiliary hot roll, and water for cooling roll. It also has various helpful accessories of operating instruments, and electrical controls.

shown in Figure 35. The roll of base paper is supported on a roller at one end of the machine. From this roller it is led through a trough containing the wax that is kept molten by a suitable heating device. As it leaves the trough, scraping devices remove the excess wax and control the film thickness. The sheet than passes over chill-rolls, which set the wax, and on to the rewinder. Depending upon the requirements the rewound coil is either sheeted or cut into specified widths on a slitting machine (Figure 36).

In the printing of colored illustrations for magazines there is apt to be an offsetting of the colored inks to the white sides of the sheets as they are piled freshly from the press. By mechanically spraying the sheet with a fine cloud of wax by a Grammer spray machine this offsetting is avoided. The type of wax required is one that is hard so that the droplets are not flattened and smudging is avoided. It may be brittle, that is, hard, but low in tensile strength.

Wet Waxing. Coating compositions for paper and paperboard to improve the appearance of the printing and to improve water resistance of coated sheet have been developed by the American Cyanamid Company, according to British patent specification 594,301 (Nov. 7, 1947). One composition (A) comprises domestic coating clay 240, sodium tetraphosphate



Courtesy Charles Beck Machine Co., Phila., Pa.

FIGURE 36. Razor blade slitter and rewinder.

1, enzyme-treated starch 60, water 273, and acid-stable wax emulsion (50% solids) 12 parts by weight. The wax emulsion is composed of *crude scale wax*, water, and a gum emulsifying agent. Another coating composition (B) calls for domestic coating clay 240, sodium tetraphosphate 1, enzyme-treated starch 60, water 273, acid-stable wax emulsion 12, urea-formaldehyde polymer (dry basis) 12, and ammonium chloride 1.8 parts. The latter salt acts as a catalyst for the urea product. It can be thinned if desired by the polyphosphate dispersing agent. An effort is made to get a pH of 6.6 to the final composition.

When a soda stock is brush coated with the composition, the paper so coated is cured for 10 minutes at 70°C (158°F) and then supercalendered. With composition A the "wet rub reflectance" is 13 per cent and "curl when wet" is 59°C. With composition B the figures are 5 per cent and 20°C respectively. Coating composition may be applied to paper stock suitable for the production of printing and labeled paper, identification tags, wall paper, insulation and wall boards, box board and container board, flour bags, and the like.

Moistureproofing Cellophane. Sheets or films of plasticized regenerated cellulose, namely cellophane, a nonfibrous material, by virtue of

their transparency and flexibility, have attained extensive and widespread use as wrapping tissues. Cellophane produces a package which, in addition to being extremely attractive, clearly displays the article or material wrapped. Plain transparent regenerated cellulose sheeting (P.T. Cellophane), however, has one serious disadvantage, namely, it is not moisture-proof. In order to make cellophane more widely applicable to wrapping foodstuffs, drugs, tobacco products, and other items, Cornwell[36] proposed a transparent coating with a cellulose resin base, one which will adhere to the base sheet so that the coating and the sheet remain inseparable. Cornwell's coating is prepared from a cellulosic lacquer base, plasticizing resin, plasticizer, and wax, together with a solvent. Very little wax is used in the coating composition. Charch and Hershberger[28a] accomplish a similar result with a composition of cellulose lacquer base, pale crepe rubber, and *paraffin wax*; the latter is the chief constituent. In general, the moisture-proofing compound in use is a mixture of nitrocellulose lacquer, plasticizer, paraffin wax 149/150°F (AMP), and a solvent.

Cornwell[36] specifies a lacquer base of nitrocellulose, cellulose acetate, benzylcellulose, or a film-forming synthetic resin. The plasticizer is dibutylphthalate or its equivalent; the wax a hard wax such as a paraffin of high melting point; the nonvolatile blending agent may be a blown oil like blown rapeseed, or a resin such as damar or ester gum. A mixed solvent (3.g., ethyl acetate, butyl acetate, and toluene) is used in the coating composition. The cellophane is run through the solution, excess coating removed by air knife or otherwise, and the coated material dried with regulated heat and humidity.

A claim in the letters patent of Charch and Hershberger[28a] for their coating gives the formula of the composition as pale crepe rubber 7, pyroxylin (51 sec) 10, and paraffin (m. 60–62°C) 83 parts. The coating fluid contains 90 per cent of a solvent mixture of 60 per cent toluene and 40 per cent amyl acetate. They specify a coating on both sides of 0.00001–0.00015 inch total thickness in the dried state. The cellophane so coated may be heat-sealed by means of a hot iron in two or three seconds, making the wrapping tissue easily amenable to many types of packaging. In the case of the Cornwell coating previously described, the sealing is effected by the application of methyl "Cellosolve," methyl acetate, acetone, etc.

In 1939 Charch[28] patented a simpler coating composition for cellophane comprising a plastic or plasticized resin and wax or waxlike substance, omitting a cellulose derivative as a constituent. The resin-wax mixture is dissolved in an adequate amount of toluene or appropriate solvent. The improved packaging material is obtained by combining, impregnating, coating, or spraying the cellophane sheeting.

Examples of the coating composition include (A) vinyl resin 15, tri-

cresyl phosphate 3–7, *paraffine* 1–3 parts; (B) styrene resin (polymerized metastyrene) 9, tricresyl phosphate 4, *paraffine* 2 parts; (C) alkyd resin 15, *paraffine* 1, and castor oil 1.5 parts; (D) gum mastic 5, white *beeswax* 2, *paraffine* 2, and toluene 50 parts. The vinyl resin is the copolymer of vinyl acetate and vinyl chloride. The alkyd resin is prepared from glycerol 14.6, phthalic anhydride 20.7, rosin 33, and tung oil acid 31.0 parts. The patent covers both article and coating composition.

Trade designations such as "Cellophane MAT" and "Cellophane MSAT" refer to cellulose-lacquered and heat-sealing coatings respectively.

Moistureproofing Laminated Wrapping Material. Both fibrous and nonfibrous materials are laminated to textile fabrics or to metal to suit various packaging needs. The wrapping of ordnance has provided the largest use for microcrystalline waxes during World War II. For example, the wax coating of cellulose acetate on scrim is used for Type I demanding a high bursting and tearing strength to the wrapping of metal parts, etc., as outlined in "Wrapping, Greaseproof U. S. Army Spec. No. 100–15, issued 10 Feb. 1944." Type II calls for a medium bursting and tearing strength which is met by waxed acetate on kraft. Type III calls for a low strength, which is met by waxed cellophane and scrim. Microcrystalline waxes are also used for "AXS-1015 Wax Dip Coating" of same or like specification. Metal foil suited to wrapping foods and other commodities may be coated with thermoplastic which has *petroleum ceresin wax* in its composition, at a temperature above that of the melted mixture, and according to Laufer[103] then lacquered to prevent offsetting, and without destroying its heat-pressure sealing efficiency. The aluminum foil used in laminating to a kraft paper undercoated with moistureproof material can be of the order of only 0.0005 inch thickness. Such a laminated wrapping material with the foil on the outside is used for wrapping machine parts.

Termite proofing of food packages is effected by adding to the wax used in waxing the paper a suitable chemical compound such as hexachlorocyclohexane; DDT; 3,5-dinitro-*o*-cresol; and its salts with phenothiazine and acetic acid. The insects, such as damp-wood termites, are prevented from boring through the waxed paper treated with the chemicals.

Waxed Drinking Cups. A drinking cup made of paper material is a receptacle ordinarily used for temporarily holding water. It is made in rigid cup form, or flat, resembling a small envelope. Drinking cups are made of bleached sulfite, generally paraffined on one side. The paper is hard sized and of medium to heavy substance made on a fourdrinier machine. With the advent of sanitary codes of the municipalities in the United States the paper cup became a public necessity. Water cups are of various shapes: conical, wedge, seamless (1-piece), and 2-piece flat bottom, generally holding 3 to 5 liquid ounces. Cold drink cups, except wedge, are also made in

6 to 24 oz sizes. Portion cups are the smallest, ranging from 0.5 to 5.5 oz, and are seamless. Flat-bottom cups (Dixie type) are made with plain or pleated walls. Cone-shaped cups (Vortex type) are made from waxed paper.

The customary procedure in a plant making flat-bottom drinking cups (Dixie type) is to slit the paper to the desired width, rewinding it into the narrowed width rolls, which are fed to machines which colorprint designs or wording. The printed rolls are then mounted on spindles of the cup-making machines, which die-cut the strip into sections, each section constituting a cup body. The body is formed and glued on a mandrel. Another strip fed into the machine is die-cut into bottoms. The formed cups are transported to waxing machines. The cups are placed bottom-up on belt conveyors which carry them through a wax-spray booth at the end of the machine. The sprays of wax (at 250°F) come from many directions, so that all cup surfaces are adequately covered with wax. The speed of cup travel (100 or less per minute) through the spray booth determines the thickness of the wax film. After leaving the booth the cups travel through a covered heated zone (at 180–200°F) which causes the wax to penetrate the paper. Cups for vending machines must be dry-waxed by longer zone heating to preclude their nesting in the machines.

The seamless pleated cup (Lily cup) is made from a circular piece of waxed paper which is formed by a plunger forcing the paper into a die. (*Esso Oilways*, Nov., 1949). Hot-drink cups are not customarily waxed but made in tumbler and squat broad-based container types from specially sized paper. However, recently there has been a measure of success in producing waxed hot-liquid cups by employing high-melting synthetic waxes.

Of the 7 to 8 billion waxed containers consumed per year about 5 to 6 billion are cups for cold drinks and water.

In the manufacture of paper cups, particularly for those types used for warm liquids, it becomes necessary to use a wax of an adequately high softening and melting point. Reifsnyder[141] in a patent assigned to the Tulip Cup Company suggests that paper receptacles be impregnated with a compounded wax comprising *carnauba* and *paraffin waxes*; e.g., carnauba 20, and paraffin 138/140°F (AMP) 80 parts. Since the melting point of carnauba wax is about 180°F, the compounded wax would melt at 160–170°F.

One of the more recent additives to the paraffin is polyethylene wax. With a polyethylene of 1800–1900 molecular weight the addition of 4–5 per cent to paraffin of 149–151°F (AMP) grade will give a clear melt at 185°F, softening point 140°F, and blocking point 120°F minimum. The viscosity is about 52 (SUS 210°F), and the wax can be sprayed on the cups. A mixture of paraffin, microcrystalline, and polyethylene waxes, may also be used to produce a superior high melting coating wax for coffee cups and the like. The use of polyethylene wax of less than 4000 molecular weight has

met with favor because of the ease with which this wax can be incorporated in the paraffin or other petroleum wax. Synthetic paraffin waxes, made by the Fischer-Tropsch process, with melting points of 105°–110°C, may be used to advantage in impregnating paper cups to resist very hot liquids.

There are 12 or more manufacturers of paper cups in the United States. The annual value is said to exceed $50 million. Paraffin wax represents 10 to 20 per cent of the container weight. Over 20,000,000 pounds of paraffin wax are used annually for the wax processing of paper cups. In addition about 250,000 pounds of other waxes are consumed.

Waxing Paper Containers. Paper, strawboard, and like containers are impregnated with wax by dipping them in a bath of melted wax kept at 190–200°F temperature. Usually the containers are maintained in the bath for about 30 seconds, and then are suspended about 10 seconds to drain. In their manufacturing production line as described by J. Spicer & Sons[96] the containers are placed in cages pivotally suspended between endless chains, and are moved horizontally through a bath of melted wax, and through an inclined path to permit draining before discharge. The cages consist of U-shaped supports carrying a base of netting or like material, and a hinged lid or cover resting on adjustable nuts on the supports. The lis is raised to allow containers to be fed to the cage by engagement of projecting arms on the lid with brackets fixed to the front of the machine. The cage is tilted to discharge the containers by arms engaging a bar at the rear. The bath is adjustable vertically and is heated by burners or by a steam coil[95].

In Reed's process[139] a paper container, fabricated from a white bleached sulfate or other suitable taste-free paper base, is subjected to a moisture-proofing material at a temperature at least as high as 212°F, so that the paper is impregnated. The container is then subjected to a bath of paraffin wax at a temperature below 212°F, when it is later chilled and made ready for use. This method has come to be known as a "double wax dip," and has been extensively employed in the waterproofing of cartons used for army rations, ammunition, and dehydrated foods shipped overseas from the United States. Over 60,000,000 pounds of petroleum waxes are consumed per year for such purposes.

Containers for cheese, butter, and ice cream must be liquid tight. The liquid-tight container is made of a fine grade of bleached sulfite of sanitary quality, and usually coated with wax after it has been colorfully decorated. Over 5,000,000 pounds of wax are consumed annually for waxing containers other than paper cups.

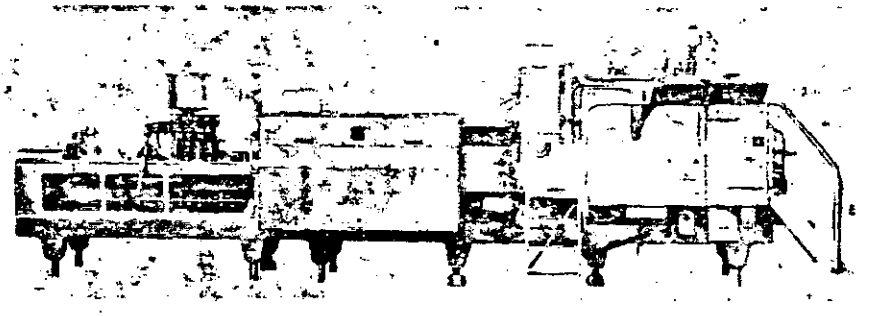
Paper Milk Cartons. More petroleum wax is consumed in coating fiber milk containers than for any other known item. In 1939, 450 million one-trip paper milk bottles were coated with paraffine, in the United States.

Since then the production of paper milk containers has increased several fold. In 1947, 116,000,000 pounds of paraffine were used for the purpose, and at the present time the consumption is reported to approach 550,000,000 pounds.

Paper milk cartons are supplied to the dairies in either the prefabricated and waxed form ready for filling, or in a "knock-down" form to be assembled, waxed, and filled on a Pure-Pak machine.

Cartons fabricated of white bleached sulfate (bleached kraft) paper in the past have been double-waxed to make them waterproof. In the prefabricated carton the body blank, which is printed by letterpress in colors, is coated at the edge on three sides with a plastic-resin adhesive. The ends, one of which carries a staple attached pouring spout, are coated on the edges with adhesive, waxed, and later inserted in the square folded carton body, the fastening at the seam and at the ends being automatically done with mild heat and pressure.

The first dip in paraffin wax of the paper carton material is done with a low melting paraffin wax (128/130°F—AMP) at a high temperature (about 212°F) for the purpose of impregnating the paper. The second dip of the carton is carried out by total immersion in a wax bath for a matter of a number of seconds time when it is automatically upended and permitted to drain out the excess wax. The wax is of about 133/135°F melting point, modified by a very small percentage of microcrystalline wax. The coating temperature is somewhat above 147°F. The wax coating, which is of substantial thickness, prevents the wicking action of loose fibers, makes the container milkproof, renders it taste free, and gives the carton added wet strength to make it suitable for packing with ice.



Courtesy Ex-Cell-O Corp., Detroit, Mich.

FIGURE 37. A machine for continuous automatic packaging of milk in waxed cartons. Flat blanks, printed and diecut, are placed in the machine, which then forms, hot paraffines, sterilizes, chills, fills, seals, and dates cartons of milk at the rate of 75 per minute. This model is known as Senior Model "Q" Pure-Pak milk packaging machine.

However, only one coating of wax, such as paraffine with anti-oxidant added, is applied to a carton such as "Pure-Pak," which is shipped to the dairies in a "knock-down" form to be assembled, waxed, and filled on a Pure-Pak machine. The wax thus used is generally one of 133/135°F melting point modified by a small percentage of microcrystalline (1–3 per cent) and with or without the addition of a very small amount of synthetic wax to improve gloss and other physical characteristics (see Dairy Wax, p. 502). Some users effectively add 0.1 per cent of asphalt to the wax as an anti-crystallizing agent, without interference with the color of a cream-colored milk container. The Pure-Pak carton has a square shape with a gable roofed top.

Waxing Ration Boxes. The Quartermasters Corps of the U. S. Army specify the use of a blend of paraffin and microcrystalline types of waxes for wax dipping the K-ration or field ration boxes. The packages after dipping are drained in an angular position to eliminate accumulation of wax on edges. These are the individual ration packages which hold concentrated foods and are generally very small in size.

A double wax dip method for waterproofing cartons of rations, ammunition, and dehydrated foods is adopted. The impregnating is often done with refined paraffin to which has been added slack wax or petrolatum, while the finish dip is made with the wax blend. Microcrystalline petroleum wax has proved advantageous for military packaging because of the high melting point obtainable and its great ductility which prevents chipping at low temperatures. Petroleum waxes in themselves do not provide grease-proofness.

A paraffin wax of 138–140°F (AMP) grade and a micro wax of 140°F (AMP) may be blended advantageously. The resultant wax will have a penetration value (100 g/5 sec/25°C) of about 13, will be both flexible and tough, and will not become brittle at low temperatures encountered in actual use.

Liners for Jar Closures. Metal or plastic closures for bottles and jars are customarily lined with a disc comprising a cushion material made of newsboard, white pulp board, composition cork, or felt. The cushion piece is invariably faced with a thinner protective facing material or membrane consisting of metal foil, plastic film, coated paper, or simply wax. The cushion material itself is often impregnated with wax to make it less absorbent of liquid.

The protective facing material can be an oil paper, varnish-coated paper, vinylite-coated paper, "Pliofilm," saran, polyethylene, glassine, or something else. The cheapest oil paper liners are simply coated with fully refined *paraffin wax*; varnished paper liners are usually coated with an artificial *ceresin*, and composition cork with either *paraffine* or *beeswax*, the latter

if resistance to oil is needed. Nonslip waxes are used for solid liners in lug caps and the like.

Various waxes are used in bottle cap liners to meet specific requirements in accordance with the type of product for which the cap is provided. The waxes include paraffin of 128–130°F or higher melting point, microcrystalline wax of 160°F or higher melting point, ozokerite, and yellow beeswax. One of the harder waxes, such as carnauba, candelilla, "Castorwax," "A-C Polyethylene Wax #6," etc., is often blended with the softer wax to improve its physical characteristics. In general it is desirable to use waxes of high melting point in caps for glass jars, as the containers are often filled with a warm product, or after filling are washed with warm water, and it is necessary to avoid having the wax stuck to the lip of the glass.

"Wax plastic liners" generally consist of wax-saturated pulp board which has been faced with a relatively thick coating (0.007–0.012 inch) of wax of high melting point. Film liners such as vinyl (copolymer of vinyl acetate and vinyl chloride) may have the wax already incorporated in the resin mix before it is applied to the paper facing material. A waxed paper liner for sealing mineral water may be made by coating sulfite paper with *paraffine* 17, and *ozocerite* 13 parts. A waxed varnished paper may be produced by coating the varnished paper with a mixture of *paraffin wax* 60, *microcrystalline wax* 38, and *carnauba wax* 2 parts. Innumerable modifications of such formulations are made to suit the particular uses of jar closures, in accordance with the type of closure and the type of product on which the closure is to be employed.

Rogers and Ebert[141a] proposed the use of a closure-liner material which exhibits thermoplastic properties and strong adhesion to metal as well as cellulosic surfaces, after cooling. It consists of 40–50 parts of paraffin wax, and 50–60 parts of butyl rubber. The latter is produced by the low-temperature catalytic polymerization of isobutylene with butadiene and isoprene.

Wax-Resin Coatings for Paper and Cloth. Mixtures of resin and wax provide thermoplastic coatings for cloth, as well as paper. Paraffin wax, microcrystalline wax or both, blended with *vinyl-copolymer resins, acrylic esters*, or *rosin derivatives* are customarily used in coating cellulosic materials. Corkery and Burroughs[35a] discovered that a glossy composition for protectively coating material may be inexpensively prepared by combining a terpene resin with paraffin wax. The paraffine and resin are compatible and yield a homogenous mixture having a much higher melting point than the paraffine itself, and yet possessing distinct waxy characteristics.

Terpene resins are made by polymerizing selected unsaturated constituents of gum spirits or turpentine, polymers of beta-pinene, and the like. A paraffin wax of about 140°F melting point is preferred. The blending of

terpene resin and paraffin wax greatly enhances the resistance to abrasion and provides heat-sealing properties better than the wax taken by itself.

Ceresin wax, candelilla wax, carnauba wax, montan wax, and other waxes can be blended with terpene resins, but high melting *paraffine* is generally preferred. A composition of the sort described can be prepared by fusing together paraffin wax 90, terpene resin (300°F—M.P.) 10 parts. It has a higher gloss and less opacity than paraffin. A composition capable of rendering paper transparent and giving it a glossy finish, so that it is well suited for the packaging of foods and the like, may be prepared from a mixture of terpene resin (275°F—M.P.) in a proportion of 30 per cent and more of the resin.

Polyethylene-Wax Composition. Schneider *et al.*[145a] proposed that paper or fabric be coated with a three-component solid solution mixture of wax, polyisobutylene, and polyethylene to make it waterproof. The polyisobutylene and polyethylene are milled together, and the mixture placed in a hot kneader, whereupon the molten wax (e.g. paraffine) is added, dropwise at first and then at an increasing rate. The mixture melts at 120–150°C, is readily absorbed by the paper, and gives a strong heat seal in the wrapper. Stacked sheets thus coated show little tendency to "blocking."

Artificial flowers and artificial fruit may be impregnated to improve water-resistant properties and to impart a translucent finish, by the hot-dip coating of Moore[118a], which consists of a mixture of *N-o*-xenyl stearamide 37, microcrystalline-petrolatum blend 60, and hydrogenated rosin 3 parts.

In the manufacture of window envelopes the transparentizing material consists of a mixture of rosin and *paraffin wax*. It is applied to one surface only of a sheet of paper; heat is directed to the same surface until the material melts and penetrates the paper, while simultaneously circulating air along the opposite side of the paper, and thereafter permitting the sheet to cool and the transparentizing material to cool.

Polyethylene and Polyisobutylene Plastic Wax Films. *Paraffin wax* can be blended with a small amount of polyisobutylene, and the polymer-wax blend applied to cellulosic or noncellulosic transparent film material to produce transparent airtight wrappings for cheeses, etc. The ends of such wrappings may be readily sealed by slight heat and pressure. Polyisobutylene is known as "Oppanol" when made in Germany, and as "Vistanex" when made in the United States. The polymerization is conducted by the refinery at a low temperature with the aid of boron trifluoride as a catalyst.

The wrapping material known as "Parafilm" has an underlying cellophane sheet, or the like, on which the wax compound is coated. "Parafilm"

can be printed on the unwaxed side, and provides a very flexible sheet for wrapping, and one which can be heat sealed for the protection of various articles of food, such as cheese, etc.

The coating to the film material, such as MAT cellophane or glassine, may be applied by the method of Abrams and Wagner[5] in which the transparent sheet is made to pass between a lower heated cylinder and an upper cylinder. The distance between the two corresponds to the desired thickness of the coating. The task of the upper cylinder is to spread to the coating evenly on the base material. Immediately following these two cylinders is a third one; this cylinder is water cooled and its purpose is to solidify the applied coating so as to permit immediate rewinding of the finished sheet material.

Polyethylene, which is a high polymer, was originally extruded in a tubular form but later in a continuous sheet form. This material, because of its very low moisture penetrability property, has been extensively used in packaging food and other material. More recently the packaging utility of polyethylene has been greatly extended by using polyisobutylene as a plasticizer to it. The two polymers are completely compatible. Newberg[123] gives the following formula for calendered and extruded sheets: Polyethylene-polyisobutylene blend 100, "Deenax" 0.25, stearic acid 1.0, and *microcrystalline wax* 190°F AMP 2.0 parts. "Deenax" is a nonstaining, nontoxic inhibitor (to breakdown of polymers) sold by Enjay Company Inc.

The water vapor permeability (g/24 hr/100 sq in., 100°F) and relative cost per unit area of cellophane is given by Newberg[123].

Packaging Material	WVP	Cost (Cellophane = 100)
"Pliofilm" (Grade FF)	2.5	174
Waxed sulfite	0.5–1.5	44
Polyethylene	0.9–1.2	122
Lacquered glassine	0.5	104
Wax-laminated glassine	0.5	139
MSAT cellophane	0.3–0.8	100
Waxed glassine	0.2	70
Saran	0.2	291
Polyethylene-polyisobutylene	0.2–0.3	122
Metal-foil laminate	0.0–0.3	300

The base resin used in the polyethylene-polyisobutylene blend referred to is the polyethylene known as "Du Pont PM-1," and the plasticizer a polyisobutylene B-120 (120,000 m. wt., Staudinger). The base resin and plasticizer in this instance were in the proportion of 50:50. Good physical properties are retained by those blends containing up to 40–50 per cent of polyisobutylene. The physical properties referred to include tensile elonga-

tion, heat resistance, low-temperature flexibility, gas permeability, water vapor transfer, chemical resistance, processability, and heat sealing.

Abramowitz[1] has reported on tests made with parchments and glassines in which 5 pounds to the ream of a blended wax comprising *paraffin wax* and 5 per cent "Arwax 612-5" were applied on one side of paper. A good heat-sealing quality could be obtained, and the coated wrapping papers will withstand low refrigerating temperatures without becoming brittle. No flavor is imparted to the food. The results were somewhat variable in other respects, such as stainproofness, greaseproofness, and waterproofness. Sulfite paper (25 lb per ream) coated with a blend of *paraffine* 135° M.P. and 3.8 per cent of "*Arwax*" (equivalent to 1% polyethylene in finished coating) have shown water vapor penetration values of about 0.3 for the uncreased and 1.65 for the creased paper. Under practical conditions of wrapping foods the waxed paper is assigned a WVP value of 0.614 against 0.817 for 0.001 inch thick polyethylene film, or 0.313 for 0.004 inch film as controls. The tests were made at 100°F and 95 per cent R.H. covering a period of 3 days, with sample sealed to a container of calcium chloride placed in a cabinet.

Polyisobutylene-Resin-Wax Blends. Resin is used with polyisobutylene and wax to increase the hardness of the wrapping film. Resin also increases the luster and permits the film to be handled without its "blocking." Various commercial resins are useable for the purpose, e.g., "Nevellite," "Staybelite," "Aroclor," "Damar," etc. An example of a "Vistanex"-wax-resin composition for coating film is the following: "Vistanex" 10, *paraffin wax* 35, and resin 55 parts. The preferred paraffin is one with 134–136°F melting point. The "Vistanex" is a product of the Standard Oil Development Company, Linden, New Jersey, and can be dispersed in a manner similar to wax rubber dispersions. Buna S, which is a polymer butadiene compounded with a lesser amount of styrene, and a little *stearic acid*, can also be blended with wax and resin, but not so readily.

In the Thomas process[161] the polymer of butylene (m. wt. 50,000–100,000) to the extent of 5 to 15 per cent is dissolved in a hydrocarbon solvent and then homogenized with *paraffin wax*; the homogenizing is carried out in an attenuated stream subject to a substantial centrifugal force, and the solvent later removed by heat and vacuum. The "Tervan Waxes" with attached number designations of the Enjay Company are blends of polyisobutylene polymers with *paraffin* or *microcrystalline wax*. The polyisobutylene constituent is usually a blend of a softer and harder base resin, selected from a group of B-80, B-120, and B-200, the numbers designating the molecular weight when multiplied by 1000. The polyisobutylene-petroleum wax base waxes in turn can be blended with relatively large amounts of hydrocarbon waxes (e.g., paraffine) to produce compositions applicable to coating cellulose material to make it moistureproof, gasproof,

refrigeration resistant, flexible, heat-sealing, etc., applicable to the packaging industry.

Carbon Papers. The principle generally used in the manufacture of carbon paper, also called "carbons," is that of coating one side or both sides of a paper material with a copy ink, which is a mixture of wax, dyestuff, pigment, and vehicle or plasticizer. The amount of copying carbon composition applied to the paper is regulated to such a proportion that when the sheet is placed downwards over white paper and beneath the sheet upon which the writing or typing is done, the color may be transferred by the pressure of a pencil, pen, or type to the lower sheet, and an exact copy of the writing obtained.

Theoretically speaking, the ideal carbon paper ink, according to Olsen[125], would be one made from a wax-carrying color, and containing no oil. Such a formulation would not be practicable as the finished composition would be too hard to release an impression. Therefore a precise balancing of the three ingredients, oil, wax, and color, must be brought about to yield an ink with the desired characteristics. Oils are chosen for their nondrying properties (e.g., mineral oil), since it is very important that the oil will be resistant to both drying and oxidation; otherwise the coated carbon sheet will harden in the course of time, and refuse to release a marking. The prime function of the oil is to produce softness and compactness of the ink, whereas that of the wax is as a vehicle to carry the color, and keep the ink from completely soaking into the paper.

Inert material such as china clay, or fuller's earth is quite commonly used in conjunction with the oil, wax, and color ingredients of the ink foundation.

Carbon paper ingredients are mixed in roll, pebble, or grinding mills. After hardening and remelting in steam-heated kettles, the fluid is poured into coating machine reservoirs. Tissue paper unwinding from a spool is coated by a drum which picks up the mixture from the reservoir. It then passes through a dryer and is rewound on another spool. Carbon papers are generally hand-cut into large sheets and recut by machine into standard sizes.

Type of Paper for Carbons. For "pencil carbons" dark blue, red, or more commonly magenta papers have largely superceded white paper of rag and chemical pulp. For "pen carbons" only tinted rag paper is used; and in the case of "types," carbons for typewriters, the paper must have a texture so as to receive the blow the type uniformly and yield clear imprints without the application of undue force. The carbon coating is applied to tissue paper of 4, 5½, 7, and 10 lb wieght (20 x 30, 480), of close texture, smooth surface, free from pinholes, made specifically for the purpose. Carbon tissue is generally made of rags, manila, and jute or sulfite. It is coated

on two sides for use in sales books; lighter weights, coated on one side, are used for varying number of copies, the lighter weight being used when a large number of copies is desired. One method which has been suggested to bring about increased flexibility and longer life to the carbon is to treat the paper prior to coating with the copy ink by immersion in a solution of gutta-percha in carbon tetrachloride, and then drying.

Because the carbon paper industry is going more and more to the converter type carbons (the type that is used by the printers for the printing of carbon interleaved forms of all kinds), more and more basis weights of paper are being used in the industry. Everything from 60 to 80 lb tag stock down through 4½ lb one-time tissue is "carbonized." By type, these papers include tag board, safety check, all weights of bond paper, book papers upon which the printer actually prints, halftone, or groundwood; and all of the types of light-weight tissue previously mentioned.

Pigments and Vehicles Required. Carbon black from natural gas is used as the black pigment for certain kinds of carbon paper; hence the name "carbon." The name is retained even when the paper is coated or printed with a colored pigment. Although carbon black has a good covering power it transfers as a brownish black, and hence it must be toned by a powerful jet-black dyestuff, such as nigrosine. The carbon black preferred is one of high-color, low oil-absorption channel type. The waxy ink is referred to as the foundation, and more commonly by the makers as "dope." If lampblack is used it will comprise less than 20 per cent of the formula, whereas carbon black with oil-soluble toners might comprise 25 per cent of the dope. With a strong hue such as crystal violet the dyestuff would amount to only 3½ per cent of the mix. The dyestuff is first dissolved in double its weight of red oil. Equal proportions of wax and vehicle (oil) are used together comprising 75 per cent, or more, of the ink ingredients. The vehicle is a petrolatum oil, or a nondrying vegetable oil. Any of the higher fatty or wax alcohols are also of particular value as vehicles, e.g., *cetyl alcohol, stearyl alcohol, oleyl alcohol, myristyl alcohol, lauryl alcohol, jojoba oil,* and the like. Sesame oil is well suited to use with some of the coal tar lakes. Red is usually made from lithol or geranium lakes ground in oil. A water-soluble wax such as *"Carbowax"* has value as an ingredient in copying inks.

The Wax Foundation. The principal function of the wax is as a vehicle to carry the color and prevent the ink from soaking completely into the paper. *Carnauba wax* and *candelilla wax* are used effectively with *crude montan wax* as foundations in recipes for "dope," as the material applied to the paper is called. Crude montan wax is an excellent solvent for nigrosine. Carnauba is the most extensively used wax, followed by *ouricury,* with *sugarcane wax* now coming into prominent use. Ouricury has been a preferred hard wax for the preparation of the dope since it greatly assists

the flow of ink from the grinding mill. *Beeswax* is also used with these hard waxes to give the dope certain desirable physical properties in transfers, such as sharp imprints, that are not obtainable with the harder and more resinous waxes. *Paraffine* 128/130°F (ASTM) and *stearic acid* in very small amounts aid in producing smooth working inks, although the paraffine-stearine mixtures are being replaced by *oxidized hydrocarbon waxes*. In these wax mixtures oil-soluble toners, carbon black, methyl violet, etc., are incorporated. The vehicle is petroleum, sesame, or sperm oil. Red oil (oleic acid) is used in the cheaper dopes.

It is claimed that certain oxidized hydrocarbon waxes (e.g., OMC waxes) are of sufficiently high melting point and hardness to make it possible to eliminate a large proportion of the high melting point natural waxes ordinarily used in making the "dopes." The OMC waxes suitable for carbons have a melting point of 180–190°F, are hard, of a dark brown color, and have a density (d_4^{15}) of about 0.932. They have an acid number of about 12 and a saponification number of 30 to 40. Waxes of this kind are marketed by the Warwick Wax Company, New York, and produced at the refinery at Chanute, Kansas.

Requirements demand that the ink should exhibit little or no yield value and have a very low apparent viscosity. The viscosity is customarily measured by a Stormer viscosimeter with a temperature control of 95°C, or the temperature at which the application to the paper is carried out. Dispersion of the waxes in petroleum oils is an important consideration. Both montan wax and oxidized petroleum waxes function as dispersing agents. The dispersing properties of such waxes bear little or no relation to their acid values as formerly believed. Carnauba wax is used as a comparate when making tests for flow values.

Montan wax had lost much of the market as an ingredient in wax formulations until 1951. This was not only because supplies were not to be had during the period of 1943 to 1946, but also because when they were reinstated the imported shipments of some suppliers were adulterated with rosin. The recent availability of good grades of imported crude montan has led to a general return to its use in the carbon paper industry, to the extent of about 400,000 pounds per year. The price range is 12–16¢ per lb and an attempt is being made to capture the market with a montan product of the American Lignite Products Company, also that of the Humacid Company of California.

Brower[19] has proposed a color paste of initially porous and unglazed character in a method of forming a carbon for use in a transfer process. The color paste is comprised of an oil-soluble salt of a basic dye as its principal color constituent, a wax such as *montan* or *carnauba* wax, a high molecular weight fatty alcohol such as *stearyl* or *cetyl alcohol*, and a volatile

solvent such as carbon tetrachloride or toluene. The paste is applied to the backing.

Hattori[82] proposed a coating material for preparing carbon paper, comprising a barium soap with oil and pigment added; e.g., barium stearate 3, castor oil 2¼, and violet lake 3¼ parts. He states that soaps of aluminum or magnesium may also be used to replace the usual wax constituent of the carbon ink. However this may be, the general practice is to use wax with color as the foundation for coating paper. If Prussian blue is used as a pigment for carbon-paper inks, the blue, green, purple, or red lakes are ground up into an ink with a suitable proportion of wax and oil. Induline B-base, which is a grayish-blue color, not a true lake, is used in both typewriter ribbons and in foundations for carbons. The weighed proportions of ingredients in the ink foundation for carbons will differ according to the type and color of the paper used.

Procedure for Grinding the Dope. The manufacturer of carbon papers makes his own wax-oil-inks or dopes. The color is first introduced in the oil (e.g., white mineral oil) and the color in oil is ground into the melted wax, such as a blend of *carnauba*, *montan*, and *beeswax*. The procedure is to melt the waxes in a steam-jacketed kettle, and then transfer the melt to a steam-jacketed ointment mill, where the oil-color mixture is added. The grinding between horizontal stones is a slow process and not until the wax-oil color mixture is reground in the same or another mill, does it take on the required homogeneity or luster. One type of mill is of iron, about 18 inches in diameter, 16 inches in height to the bottom scraper, and 29 inches in over-all height. It has a corrugated, slightly convex bottom plate which can be enmeshed with the cogs at the bottom periphery of the hopper, and the degree to which the engagement is made determines the flow of waxy ink between the sand bottom plate and the revolving horizontal parallel plate underneath, the ink being removed by a stationary scraper. The ink mixture in the hopper travels by gravity down between the horizontal grinding plates, which are adjusted from coarse to fine grinding by a handset screw. The drive of the mill can be effected by means of a 2 horsepower motor. The jacket on the mill is suitable for steam pressure up to 40 pounds. The grinding plates can be easily cleaned or replaced by loosening two nuts on the side of the frame. The capacity is about 75 pounds per batch. One mill can be set below another mill, step like, to make the regrinding operation a continuous one.

The colored wax from the mills reaches a temperature of about 200°F, and while warm is run into suitable deep rectangular pans having sloping sides to facilitate removal of the solid wax-ink later. The pans are then stored until the wax-ink, or dope, is ready for use, at which time the loaves of dope are removed from the pans, broken up into chunks, and placed in

a steam-jacketed copper vessel which constitutes part of the coating machine equipment. The carbon paper machines will be described later on. The recipes for the wax-inks naturally vary as to whether the carbon papers are for typewriter or pencil copy, and there are numerous grades of each. The typewriter carbons are mostly in black, but in the "one-time carbons" blue is used to a considerable extent.

Chlorinated Rubber as Dope Ingredient. The Underwood Elliott-Fischer Company found chlorinated rubber to be of value as an ingredient of the dope, particularly as a toughening plasticizer. It tends to plasticize the wax contained in the dope in such a way as to render it tougher, with the result that the carbon gives a sharper imprint. Neidich[122] gave a formula which in actual practice produces typewriter carbon paper which is said to give highly satisfactory reproductions or copies:

	Parts
Petrolatum	42
Carnauba wax	30
Hard Synthetic Wax	10
Chlorinated rubber	10
Carbon black	14
Methyl violet	6
Nigrosine	10

The chlorinated rubber referred to is of the type known under the trade name of "Tornesit." In preparing the dope the waxes and pigments or colors are melted together and the "Tornesit" is dissolved in toluene, then added to the compound; all are ground together in a hot mill which eliminates the toluene from the formula-mix by evaporation. The completed dope is then ready for use.

Process of Coating Paper for Carbons. The tissue used for manufacturing carbon paper is a special tissue (e.g., loaded and colored) which ranges from 16 to 4 pounds per ream (20 in. x 30 in.—500 sheets). The tissue is supplied by the mills in rolls from 70 to 200 pounds in weight. Today the latter size is the normal one. The roll is placed in position at the lower end of the machine frame from which it is fed by feeding rollers through tension bars into the coating machine. Dual drives on the rolls are necessary to minimize puckering of the paper; tension bars also tend to remove wrinkles and puckers. The tissue then passes over rollers, which as they turn, bring the surface of the paper in contact with the melted dope (ink) held in a steam-heated fountain. Equalizing devices are provided to lay the ink smoothly, and feeding devices are regulated so as to give a waxy appearance to the coated surface. The equalizing roller, commonly called a jigger, was at one time a brush, but in the improved equipment designed by Mayer[115] in 1911, the jigging roll is a wire-bound rod. The size of the

From: Chem. Ind., **59**, *1* (*1946*)

FIGURE 38. Machine for carbonizing tissue and other paper material. The paper is fed from the lower roll, passing through the inking mechanism as it is wound on the upper roll. Dual drives on the rolls are necessary to minimize puckering the paper.

wire predetermines the depth of the ink coating. It was later found out that instead of a piano wire winding on the rod, the rod may have a very light groove cut to the depth of the radius of the wire. Rollers on the machine are of a kind that can either be heated by steam or chilled internally, as needed.

After the ink has been applied at approximately 95°C the coated sheet is chilled by passing it over a water-cooled roller, and wound up lightly on the receiving drum. According to Olsen[125a] a modern machine can process twelve to fourteen miles of carbon paper daily.

When making nonsmut, *hard finished carbon paper*, both hot and cold rollers come in contact with the paper. The order of the hot and cold rollers is changed when making *annealed carbon paper* (one side coated) or *double-coated paper*. Very light-weight tissues are brushed with a jigger to produce *pen carbon papers* and certain typing carbons; brushing gives a notable wave. Carbon papers that are to be gummed into manifolding books are especially prepared with selvedges.

The new carbon coating machine, "Model CC-275," of Haida Engineering Co., is so constructed that several of twelve units may be engaged in operation with the basic eight units of the machine. For example, automatic stripe carbon units, a buffing attachment, and a speedup unit are used for semicoated one-time carbons.

Lead Pencil Carbons. Lead pencil carbons are made with a cheaper foundation than is used in the typewriter carbon paper. For example, one recipe calls for carbon black 20, mineral oil 140, nigrosine base 3½, oleic acid 7, *paraffin wax* 80 parts. The carbon black is first ground with 80 parts of the mineral oil, and the nigrosine, dissolved in oleic acid, added. The hot solution of paraffin with the remaining amount of mineral oil is combined with this mixture and the whole is ground again, before spreading it on the paper at a temperature of about 110°F. In another recipe *carnauba wax*, *montan wax*, and *glyceryl monostearate* are used, the carnauba wax constituting less than 5 per cent of the coating ingredients whereas in typewriter coatings it is desirable to increase the carnauba wax to as much as 30 per cent.

Dark blue, or magenta tinted papers are carbonized for pencil carbons so as to permit 30 to 50 copies to be made without the paper showing signs of wear to the user.

Slip Resistant Carbon Paper. Attempts have been made to overcome the pronounced tendency of carbon papers to curl by coating the nonmarking side of the sheet with an ordinary waxy composition, but this aggravates the tendency of the carbon paper to "slip"—that is, to move out of place between paper sheets when put into the typewriter. A smooth typewriter carbon paper which is both slip-resisting and noncurling was invented by Kjellstrand[100a]; it involved coating one side of a thin absorbent paper sheet with a conventional copying wax, and the reverse side with an essentially similar but plain wax containing a small amount of polybutene of rubbery consistency. A few per cent of a metallic powder or other coloring material can be added to improve the appearance of the sheet, and serves to reduce surface tack without increasing the tendency to slip.

An unpigmented coating of the kind described may be prepared from (A) *carnauba wax* 38, *microcrystalline wax* (m. 68 −70°C) 10, and *polybutene wax* (paraffin type) 32 parts; or a silver-colored coating (B) from *carnauba wax* 58, *microcrystalline wax* (m. 68–70°C) 10, *polybutene wax* 32, and aluminum powder 5 parts. The polybutene wax (m. 55–56°C) employed in these formulas is a wax combination of polybutene 25, and *paraffin wax* 75 parts. The coatings can be applied in conventional fashion, using roll, knife, and intaglio coating machines; the two coatings, marking and reverse side, can be applied at once if desired. The silvered carbon paper has a very attractive appearance.

Slip resistance is also obtainable by the use of *paraffin wax* containing

ethylcellulose, combined with *sugarcane wax*, and *microcrystalline wax*. Fatty acid amides (e.g., "Armids") give both increased dye solubility and antistick qualities to carbon paper.

Mechanical Packings. Flax and cotton packings are customarily impregnated with a soft wax, such as *japanwax* or a *microcrystalline wax*. To render them impervious to steam pressure above the melting point of these waxes, an additive such as polyethylene wax may be incorporated in the microcrystalline wax in an amount sufficient to appreciably increase both the melting point and the viscosity of the packing wax.

Stencils. A stencil is a thin plate or sheet of metal, leather, paper, or other material cut or pierced with a pattern or design; this is laid upon a surface and color or ink is brushed or rubbed over it, thus leaving the ground color of the surface imprinted with the design or pattern cut out. Morton and George[119a] prepared a dry stencil by laminating a sheet of thin porous tissue coated with an impressionable waxlike material to a sheet of capacitor tissue paper 0.00025 to 0.00075 inch thick by means of an adhesive layer of plasticized nitrocellulose. The coated side of the porous tissue faces the capacitor tissue. The dry stencil described is claimed to be durable, resistant to the softening action of spirits and ink fluids, and provides a strong stencil surface which retards deterioration of the stencil during use.

Heat-resisting stencil films, according to Marran[112a], are prepared by coating cellophane sheet material with a mixture comprising mineral black 5, a nondrying oil 12, a vegetable wax 49, and aluminum powder 34 parts.

Master Carbon Sheet for Transfer. In transfer processes for effective reproduction or transfer of designs, drawings, written, and typewritten material from an original master copy, the color constituents of the ink of the carbon paper are transferred to the back of the sheet, forming a reverse copy of the design or writing. In preparing copies from this master sheet, the surface of the copy sheet is moistened with a water-miscible alcoholic liquid, which dissolves the dyes in the reverse carbon paper ink design on the master sheet, thus transferring the original pattern. In general, water-soluble dyes have been used for preparing the carbons, but they tend to soil the fingers of users and to smudge and blurr on handling. Brower[19] proposed the use of oil-soluble colors in the carbons, and oil-miscible solvents on the copy paper in the fluid process of transfer from the prepared master copy.

The dyes used in the Browder process are basic azo and amino-azo dyes such as azo-black; the azine dyes, such as the indulines and nigrosines; or the salts of basic dyes with organic acids, inclusive of nigrosines, indulines, methyl violet base, fuchsine, anthraquinone colors, and chrysoidine. Preference is given to the salts of the higher fatty acids, such as stearates,

oleates, palmitates, laurates, and abietates as the sole or principal color constituents in the carbon paper coatings, or transfer inks. Nonaqueous fluid transfer liquids are the lower alcohols, glycol ethers, the lower ketones, acetone, ethyl methyl ketone, and many hydrocarbon and halogenated hydrocarbon solvents. The solvents are applied in the usual manner on a suitable duplicating machine which transfers fluid to applicator roll to dampen the copy paper.

The waxes used for the carbon foundation for a master carbon sheet have a melting point within the range of 50 to 100°C and have in the past been selected from the following: halogenated napthalenes, carnauba wax, sugarcane wax, japanwax, montan wax, ouricury wax, etc. It is quite probable that the harder *petroleum ceresins* might be effectively used. Modifying agents are generally selected from a group of alcohols, which includes *cetyl*, *stearyl*, *oleyl*, *lauryl*, and *myristyl*. These agents lessen the stickiness and tackiness of the dye mixture applied to the carbon paper. Mineral oil is similarly used. A commercial mixture of some of these alcohols—stearyl, oleyl, and palmityl—is known as "Stenol." Examples of formulations are as follows: (a) nigrosine base B 10, stearic acid 10, "Stenol" 10, montan wax or "Halowax" 2 parts; (b) methyl violet base 10, stearic acid 10, "Stenol" 10, and carnauba wax 2 parts; (c) nigrosine base N 10, induline base B 5, spirit-soluble nigrosine jet 10, stearic acid 5, carnauba wax 8, mineral oil 13, and triethanolamine ½ parts.

Wax in Typewriter Ribbons. The manufacture of typewriter ribbons and of carbon papers are usually associated; however, there is little in common between the two except that both have a transfer ink and are used on typewriting machines. Typewriter ribbons are made by inking a closely woven spun silk, rayon, or cotton fabric tape wide enough to produce a number of ribbons when sheared to the specified size. The ink used for charging the ribbons is applied by a brush jigger or porous wiping roll to the tape from ink supplied by a fountain of the inking machine, as the tape is pulled through the feeding rolls at a rapid speed. The tape may be lacquered on the rear side with a coating which is permeable to ink, but prevents excessive flow. The inked tape is then sheared with rotating knives. The ribbons are automatically cut crosswise to metered lengths and spooled.

Ribbon inks are made to a thin paste-like consistency. They consist essentially of pigment ground in a nondrying oil like rapeseed with the addition of an oil-soluble dyestuff, and a water-soluble mineral salt or a glycol ether which can be oil dispersed; the make up of the ink being similar in principle to that of a copying ink. These water-soluble additives permit the use of increased color-oil ratio and improve the smoothness and fluidity of the paste.

Black ribbon ink is made by grinding lampblack in oil and toning the

color with nigrosine and induline bases. Purple ink is made by grinding a methyl violet lake dispersed in oil with a base of methyl crystal violet dissolved in oleic acid. Blue ink is made from a blue lake ground in oil and combined with Victoria blue base dissolved in oleic acid. Red is made from lithol or geranium lake ground in oil. The additives, which are sometimes referred to as lustering agents, include *"Carbowax"* as well as some of the glycol ethers. Murphy[120] recently recommended the use of sodium decyl sulfoacetate, sodium monoethyl succinate, and similar compounds to the extent of 0.5 to 2.5 per cent of the concentrated color paste composition. There is an increasing tendency toward incorporating small amounts of resins and synthetic waxes in typewriter ribbon inks to lend both body and luster to the impression.

Carbonless Transfer Paper. Carbon copies without carbon paper are made possible by the recent development of chemically treated papers with a duplication system capable of turning out four hand-written copies simultaneously or as many as seven with an electric typewriter.

Chemically treated duplication papers are prepared in two steps. First, a rupturable solid film of colorless wax binder carries minute droplets of a colorless recording oil and a color-reactant material. When the film is broken by the typewriter or pencil stroke the oil droplets with their colorless oil-soluble dye derivative are released. The recording oil is transferred to the undersheet of a specially sensitized paper in a manner similar to the way in which transfer of coloring material is made from a carbon transfer sheet onto an undersheet, except that the wax is colorless and plays no part in causing a mark on the undersheet, the only color-producing material being the color reactant carried in the oil.

The acid-like sized attapulgite or other adsorbent mineral coating of the undersheet in contact with the color reactant carried by the oil acts as an electron accepter causing color to appear.

In the field of sales books a duplicate copy of a sales entry is made on the underlying sheet by means of a manifold transfer coating. The manifold sheet which constitutes the original entry will have on its back the transfer coating but is colorless, will not be rubbed off by wet hands, and may be safely placed with white merchandise without smudging it.

According to Davis and Thacker[42a] the following waxes may be used and are miscible with the specified colorless recording oil: *carnauba*, *ouricury*, *candelilla*, *vegetable fiber*, *esparto*, *sugarcane*, *montan*, *ozokerite*, *ceresin*, *Utahwax*, *microcrystalline waxes* (170–200°F/M.P.). Synthetic waxes, such as *hydrogenated castor oil*, and *montanic acid esters* may also be used. The waxes may be compounded together to meet the requirements of hardness and smudge resistance required.

In the colorless transfer foundation about 55 per cent, by weight, of the

colorless oil containing the hydrophobic color-reactant is mixed with 45 per cent, by weight, of wax. The percentage of oil with respect to the wax may vary from 25 per cent upward. The colorless oil is a lube oil (SUS 200 sec) and the color reactant is made up of one-half crystal violet lactone and one-half benzoyl leuco methylene blue, or other suitable colorless oil-soluble dye derivatives.

Examples of suitable wax mixtures to form coatings given by Davis and Thacker[42a] are (a) sugarcane wax 4/9, fully refined paraffine 4/9, and montan wax 1/9 parts; (b) ouricury wax 22, and fully refined paraffin wax 20 parts, the wax mixture being used with recording oil 58 parts; (c) carnauba wax; (d) ouricury wax 25, and montan wax 15 parts, for recording oil 60 parts; (e) montan wax 25, paraffin wax 25 parts, for recording oil 50 parts. The wax is melted; the oil with the color reactant therein is added to molten wax, and the mixture is thoroughly stirred. This dope mixture is applied to the paper in a thickness comparable to 6 pounds of coating per ream. The coating is discernible by the texture of the surface and its light-reflecting qualities.

The principle involved in the multiple copy transfer paper dates back nearly a score of years. This is the coating of paper for impact printing, in which pressure acts to bring two kinds of substances together at the point of rupture to produce a distinctly localized mark; it is further exemplified by the modern strip label in which a colorless plastic film to receive the writing has been mounted on a color-sensitized paper. For color-forming materials in carbonless transfer paper reader is referred to the patents [Green, B. C., and Sandberg, R. W., (to National Cash Register Co.) U. S. Patent 2,550,470–1–2–3 (1951)].

WAXES IN PHARMACEUTICALS

Waxes are extensively used in pharmaceutical preparations known as cerates and ointments, where they serve as a means of bringing the medicament in intimate contact with the skin. Waxes are also used to some extent in suppositories and in the enteric coatings of pills.

Cerates. The United States Dispensatory defines a cerate as an unctuous substance consisting of oil or lard, mixed with wax, spermaceti, or rosin, to which a medicament is frequently added. The following is quoted from this same authority. "Their consistence, which is intermediate between that of 'ointments' and that of 'plasters,' is such that they may be spread at ordinary temperatures upon linen or leather, by means of a spatula, and do not melt or run when applied to the skin. In preparing them, care should always be taken to select the oil or lard perfectly free from rancidity. In reference to the wax, too, there would seen to be a choice, as experience has shown that cerates made with yellow wax keep longer unchanged than

those made with white or bleached wax . . . The liquefaction should be effected by a very gentle heat, which may be applied by means of a water bath, and during the refrigeration the mixture should be well stirred, and the portions which solidify on the sides of the vessel should be made to mix again with the liquid portion, until the whole assumes the proper consistence, or, as some prefer, the melted cerate is allowed to cool quickly without stirring. When a large quantity is prepared, the mortar or other vessel into which the mixture may be poured for cooling should be previously heated by means of boiling water. It has been proposed to substitute paraffin for wax in the preparation of the cerates, but the great tendency to produce granulation in the finished cerate has largely prevented its use."

Cerates differ somewhat from ointments as the cerate consistency is especially suited for spreading on linen, while that of the ointments is peculiarly adapted to inunction. *Steatinums* have the consistency of cerates but contain a large proportion of tallow. A number of the cerates were formerly listed in the United States Pharmacopoeia. The preparation *Ceratum*, or *Simple Cerate*, dates back to 1850. It consists of white beeswax 30, white petrolatum 20, and benzoinated lard 50 parts. For southern climates 5 parts of the latter are replaced by 5 parts of wax so as to hold the consistency. The U.S.P. XI gives the simple formula: white wax 30, benzoinated lard 70 parts; and cautions to preserve the cerate in a cool place. Its use was for dressing blisters, wounds, etc., the object being to prevent contact of the infected region with the air.

Ceratum Camphorae, commonly called camphor cerate, is composed of camphor liniment 10, *white beeswax* 35, white *petrolatum* 15, and benzoinated lard 40 parts. The melt is made of the wax, petrolatum, and lard, and the camphor liniment incorporated as the mixture starts to congeal on cooling. It contains 2 per cent of camphor and provides a slightly stimulating dressing. It is no longer listed in the U.S.P.

Ceratum Cantharides, or *cantharides cerate*, is prepared from powdered (No. 60) cantharides 35, glacial acetic acid 2.5 (by volume), oil of turpentine 15, *yellow beeswax* 17.5, rosin 17.5, and benzoinated lard 20 parts. The cantharides is moistened with the oil of turpentine and the glacial acetic acid, and set aside in a covered container in a warm place for 48 hours.

Melt the rosin, yellow wax, and lard, strain through muslin, and add the macerated cantharides. Keep mixture in liquid condition on water bath for one hour with occasional stirring. Finally remove it from bath and stir until it begins to congeal. The British method of preparation differs somewhat from the latter. Cantharides cerate is used as a blistering plaster. It is best spread on soft leathers, the skin being first moistened with warm vinegar. The whole art inclusive of blistering cloth, blistering paper,

vesicating taffeta, and its application in medicine, is described at length in the United States Dispensatory to which the reader is referred.

Ceratum Plumbi Subacetates, or *Goulard's Cerate*, is prepared from lead subacetate 20, *anhydrous lanolin* 20, *paraffine* 20, white *petrolatum* 38, camphor 2 parts. To the melted lanolin in a warm mortar gradually add the solution of lead acetate, and incorporate it by slow trituration. Add to the mixture the melt of white petrolatum and paraffin in which the camphor has been dissolved; mix thoroughly until homogeneous. The British method is somewhat different. The cerate is used chiefly in excoriations, burns, scalds, and chilblains, and in cutaneous eruptions. Wherever there is an acute active inflammation of the skin it is a most efficient remedy. It is no longer listed in the U.S.P.

Ceratum Resinae, or *Basilicon Ointment*, is made from rosin 35, *yellow beeswax* 15, lard 50 parts. The melt is made and strained through muslin. The British Pharmacopoeia prepares it from resin 20, *yellow beeswax* 20, olive oil 20, and lard 15 parts. The lard and olive oil are added to the previously melted resin and beeswax; the mixture is strained and stirred until cold. Basilicon ointment is much used as a gently stimulating application to blistered surfaces, indolent ulcers, burns, scalds, and chilblains. It has been said that there is no application more efficient in healing ulcers which follow burns.

Ointments. Ointments are unctuous substances softer than the cerates, made to the consistency of butter, so that they may be readily applied to the skin by inunction. Many of the ointments prepared for pharmaceutical purposes are made with a simple base to which the medicinal or potent substance is admixed. Ointments used for medicinal purposes, and which are recognized by the United States Pharmacopoeia, are labeled by the manufacturer as "USP," and must according to law conform to the USP specifications as to composition and purity.

The ointment base is known as "simple ointment," or as *White Ointment USP* (unguentum album)[165a] and is made of *white wax* 50, and *white petrolatum* 950 parts. The ingredients are melted together in a suitable dish on a water bath. Before the advent of the XIV Revision of the Pharmacopoeia, white ointment was prepared from *white wax* 50, *anhydrous lanolin* 50, and white petrolatum 900 parts. The U.S.P. XIII Revision described twenty-six different kinds of ointments, the U.S.P. XIV Revision carries twenty.

When ointments are prepared by merely mixing medicinal substances with *simple ointment*, or the like, care should be taken if the added material is a powder, that it be finely subdivided before being incorporated with the unctous matter. In some instances the powder is levigated with the petrolatum to a smooth paste, and then incorporated with the white ointment,

as for example Ammoniated Mercury Ointment USP. Similarly, in preparing boric acid ointment 5 parts of boric acid in a very fine powder are levigated with 50 parts of liquid petrolatum, and then incorporated in 850 parts of White Ointment.

Prior to the recent revisions of the U.S.P. a fine rose water ointment cream was made, in which expressed almond oil, and not liquid petrolatum, was employed as the principal ingredient. The formula of the XIII Revision wax is: *spermaceti* 12.5, *white wax* 12, liquid petrolatum 56, sodium borate 0.5, rose water 5, distilled water 14 parts, with 0.2 ml of rose oil per kilo of ointment.

Pine Tar Ointment USP, according to the XIII Revision, was prepared from pine tar 50, *yellow wax* 15, and yellow ointment 35 parts. The wax and ointment are melted together, and stirred until the mixture congeals as it cools; then the pine tar is added. This ointment has been dropped by the U.S.P. XIV Revision.

Fluid Oil-Beeswax Vehicles for Drugs. One of the preparations for parenteral administration of drugs, which complied to the requirements of the Federal Food and Drug Administration, was *Penicillin Injection in Oil and Wax*, described in the XIII Revision of the U.S.P. It is a sterile suspension of calcium penicillin in a menstruum of vegetable oil in which *white wax* is dispersed. Gradnich[73] gave a practical method for its preparation, which is as follows: Heat arachis oil (oil of groundnut, *Arachis hypogaea* L.) and *white wax* separately and filter through sterile gauze. After sterilization at 120°C for 20 minutes mix 96 parts of oil with 4 parts of wax and prepare an emulsion of 300,000 units of calcium penicillin in 1 cc. The emulsion is stable at 25°C for 1 year. A penicillin ointment USP was put up in collapsible tubes and had to be kept at a temperature which did not exceed 15°. The later Revision (XIV) defines the ointment as "penicillin crystalline or penicillin procaine in a suitable ointment base." It similarly defines *Penicillin Procaine in Oil Injection* as a sterile suspension of penicillin procaine in oil with or without the addition of suitable and harmless dispersing and hardening agents. No description is given as to the mode of preparation.

Macek[111] in 1950 assigned a patent to Merck and Company covering a fluid oil-beeswax vehicle for parenteral administration of drugs; it describes a mixture of 4.8 per cent (wt. to vol.) of *beeswax* in peanut oil which has been heated at 150–80°C and rapidly cooled with agitation. The product is anhydrous, homogenous, gelatinous, and fluid at room temperature. It is used as a vehicle for penicillin, streptomycin, and hormones for parenteral injection.

By mixing penicillin salts with a small amount of liquid *jojobaseed wax*, the salts form minute particles which are coated with the wax and thereby protected from the action of stomach fluids. The penicillin product is

covered by a patent issued to Wm. E. Hinds[83a], who states that both the liquid and solid *hydrogenated jojoba wax* can also be used as well as combinations with *beeswax*.

Analgesic Balms and Ointments. Balms are ointments used for healing or soothing, and may or may not contain medicaments. For example, a balm can be made up for the treatment of superficial burns, and formulated in such a manner that it has analgesic properties. An analgesic burn cream is prepared from *anhydrous lanolin* 30, vegetable oil 32, *spermaceti* 10, isobutyl *p*-aminobenzoate 2, and water 24 parts. The lanolin, vegetable oil, and spermaceti are melted together on a water bath and the benzoate is then added to the liquid. The water is prewarmed and added in portions with thorough agitation until it is completely incorporated. Agents which can be used to modify a lanolin base to make it softer or stiffer are *petrolatum* and *beeswax* respectively.

A balm may be prepared with a medicament which gives a cooling sensation to the skin, such as menthol, methylsalicylate, camphor, and ethyl aminobenzoate; for example, a formulation of methyl salicylate 50, menthol 10, eucalyptol 2.5, oil of cajeput 2.5, white beeswax 20, and hydrous lanolin 15 parts. The balms are filled in jars or into tubes. The medicament may be used to relieve pain by counter-irritation. For example, a chest rub may be prepared by adding pulverized mustard to a mixture of cold cream and lanolin.

The white petrolatum which is best suited for preparing many cerates, including ointments, is now obtainable in a form which is somewhat adhesive, of a melting point approaching 55°C (130°F), and outstanding in its ability to hold oils. A brand of amorphous-like soft wax known as "*Protowax*" is of this description. The United States Pharmacopoeia[165] no longer includes ointments of a greaseless kind. Such ointments are used for cosmetic purposes. (*See* Cosmetics, p. 672).

Salves. In the preparation of salves it is sometimes necessary to increase the water absorption power of white petrolatum to an appreciable extent. Ordinarily white petrolatum absorbs 30 per cent of water by weight. If white petrolatum (white "Vaseline") is melted together with 2.5 per cent of *beeswax* it will absorb 38 per cent water. If 5 per cent of the wax is employed the water absorption of the mixture is 42 per cent. Bartels and van der Welen[11b] found that a 2.5 per cent addition of *melissyl alcohol* (beeswax alcohol) will cause the petrolatum to absorb 75 per cent of water. *Spermaceti* does not appreciably increase the water absorption power of "Vaseline." The addition of 2.5 per cent of *cetyl alcohol* to "Vaseline" causes it to absorb 80 per cent water. The addition of 2.5 per cent of *anhydrous lanolin* increase the water absorption 80 to 140 per cent depending upon the rate of addition.

Suppositories. Suppositories are solid bodies of various weights and

shapes, adapted for introduction into different orifices of the human body, and usually melting or softening at body temperature (37°C). *Cocoa butter* in which a medicament is incorporated is generally used for the purpose, except when glycerinated gelatin is used. Cocoa butter is the tallow obtained from the roasted seed of *Theobroma cacao* Linné (Fam. Sterculiaceae). Cocoa butter ordinarily is brittle at temperatures below 25°C. It has a specific gravity (d_{25}^{100}) of 0.858–0.864 when liquid. It has a melting point of 34–35°C, refractive index (n 40) 1.4572–1.4585, iodine number 35–40, saponification number 188–195, and solidification point of its fatty acids of 45–50°C. Pressed butter is preferred to the extracted grade.

Certain medicaments tend to soften the cocoa butter vehicle, making it necessary to raise the melting point of the mixture and increase its firmness, which may be accomplished by the addition of *spermaceti* or its equivalent, although the finished suppository must melt at body temperature. Van Riel, Jr. and van der Wielen[167] incorporated varying amounts of cacao butter in *beeswax* (m. 32.5°C) to be used in the preparation of suppositories. They noted that the melting point falls at first, levels off at 32.6°C with 4.05 per cent of cocoa butter, and then increases to 37°C, the desired body temperature with the addition of 6.05 per cent of the cocoa butter.

Cocoa butter has the composition: oleo-α,β distearin 24.9%, oleo-β-palmitostearin 20.3%, and α-palmito-α,β-diolein 54.7%. Palmito-diolein is unstable; its iodine number drops and saponification number increases in the course of ten days.

Wax for Pill Coatings. Enteric coatings for pills—that is, coatings which permit pills to pass unaltered through the acid secretions of the stomach but which disintegrate in the intestine—contain wax or waxy substances[105]. Mills measured the efficacy of such coatings, and rated them as follows: cetyl alcohol 81 per cent, cetyl alcohol and shellac 70 per cent, and cetyl alcohol-mastic coatings 97 per cent. The coating solution of the latter type may be prepared from *cetyl alcohol* 10, mastic 10, and acetone 100 parts.

A timed disintegration and a new method of applying enteric coatings was worked out by Worton[179] and his associates. The enteric mass is prepared by melting *stearic acid* 55.5, *carnauba wax* 24.25, and *petrolatum* 1.75 parts; then powdered agar 13.9, and powdered elm bark 4.6 parts are incorporated in the melted waxes. When the mass is cool, it is ground to a powder. Before the powder is applied to the pills or tablets, they are steeped in a shellac solution and then dusted with shellac. Heat treatment with an open flame gives a gloss finish and increases the fluid impermeability of the coating. *Carnauba wax* overcomes the softening of the fatty acid and the petrolatum.

Glyceryl monostearate is sometimes used as an enteric coating for tablets. *Magnesium stearate* is used as a dusting medium to prevent pill massing. *Microcrystalline waxes* have proved unsatisfactory for tablet polishing, except where 1 part of *carnauba wax* had been blended with 3 parts of microcrystalline wax, whence the requisite polish could be obtained in 2 to 2½ hours tumbling, as determined by Kelley[100]. However, a white microcrystalline wax perfected by the Bareco Oil Company produces an excellent polish on tablets without the addition of carnauba wax. The wax has a melting point which approaches 200°F, a needle penetration of 1, and an oil content of 0 per cent; and is believed to be comprised of normal hydrocarbons in its entirety.

Powders, or tablets with layers insoluble in gastric juice, can be prepared by covering the material with a solution of shellac 5, *anhydrous lanolin* 5, and 96 per cent alcohol 75 parts; talcum is then strewn on the surface, and a coating of shellac 20, 96 per cent alcohol 80 parts is applied. The coated products are then dried at 20–22°C for at least 24 hours.

In order to protect medicaments in capsules intended to act in the duodenum from being acted upon by the stomach, a coating of *stearic acid* (m. 65–70°C) is recommended by Freeman[63]. The capsules are set upon end by means of a suitable holder and dipped into the melted acid at 85–90°C; then each capsule is reversed and set on the other end, and again dipped to produce a continuous coating. Two coatings are found to be the optimum required.

Formulations comprising *n*-butyl stearate, *carnauba wax*, and stearic acid are generally favored as enteric coatings for tablets.

WAX IN POLISHES

Polish as an article may be defined as a liquid or pasty substance for giving smoothness and gloss to the surface to which it is applied and rubbed. The field of polishes is a broad one and the polish industry consumes more animal and vegetable waxes than any other. The field comprises polishes of the following kinds: abrasive, automobile, buffing, floor, furniture, leather, linoleum, metal, shoe, stove, and miscellaneous others.

Waxes in some form or other are used in almost every type of polish. Generally speaking, a polish, has as its foundation a mass of wax, which consists in part, or as a whole, of a hard wax—one which will impart luster to the surface on which it is rubbed. The preferred polishing wax is *carnauba*, but this is frequently replaced at least in part by one of the following waxes: *candelilla*, *ouricury*, *esparto*, *sugarcane*, or a hard synthetic, or so-called replacement wax, which latter may or may not contain a proportion of natural waxes. It is customary for the polish manufacturer to combine with the harder wax a less hard and more flexible type of wax, for example one

of the following: *Beeswax, ozocerite, refined montan, ceresin, microcrystalline* or *oxidized microcrystalline* (OMC) wax, and quite often some *paraffine* to retain the solvent from rapid solvent evaporation, or to aid in the emulsification of aqueous polishes, or, moreover, to lower the cost of the wax base.

When a polish is made for the purpose of cleansing as well as polishing the surface, a mild abrasive such as tripoli becomes an essential ingredient. Polishes may be roughly classed into four different kinds: abrasive liquid (emulsion type), abrasive paste, nonabrasive liquid (both organic solvent and emulsion types), and nonabrasive paste.

An aqueous polish emulsion is usually prepared in three stages. First, the wax mass is melted. The saponifying solution is prepared separately. Second, the heated saponifying solution is added to the molten wax mass with vigorous stirring. Third, turpentine and/or mineral spirits is added to the emulsion when it is cooled. If abrasive or other agent is called for it is added with the saponifying solution.

Emulsion Polish Formulations. Emulsion polish formulations for use on linoleum, vinyl plastic, or other surfaces involve the use of a very hard lustrous wax, an emulsifying agent, turpentine and/or mineral spirits, and water. Carnauba may be used as the hard wax, but is often substituted in whole or part by a less expensive vegetable wax, a synthetic or blended wax, or by a resin. An example of a substitute for carnauba wax in aqueous emulsions is a high melting oxidized microcrystalline wax (OMC wax), which lowers the cost of formulation. An example of an emulsion polish formula is the following: carnauba 50, "Crown Wax 23" 25, "Durez 14140" 32.1, oleic acid 6.9, AMP (emulsifying agent) 6.4, sodium borate 4.0, and water 858.0 parts. "Crown Wax 23" (Petrolite Corporation) is an OMC wax having an acid value of 20–25, saponification number 55–56, melting point 180°F plus, penetration (100/5/77) 4–6, and color NPA 4–5. AMP is 2-amino, 2-methyl, 1-propanol.

The waxes, resin, and oleic acid are melted at a temperature not exceeding 270°F and cooled to 210°F with agitation; the AMP is added with stirring at 200–210°F, followed immediately by sodium borate in a saturated solution. The mixture is cooked at 200–210°F for five minutes; then slowly poured into water at 200°F with rapid agitation. When the emulsion has smoothed out, a cold solution of "leveling agent" is added during agitation and cooling at room temperature. The leveling agent which is either a solution of shellac or amberol is employed to decrease tack, increase film hardness, and increase slip. The formulation as given requires about 12 per cent of leveling agent. Low-cost polishes can be made by substituting the OMC wax for carnauba, and greatly increasing the amount of leveling agent, up to about 50 per cent. Refined *ouricury* may replace carnauba

wax, and morpholine may be used as an alternate to AMP, in emulsion polish formulations.

Automobile Polish. Typical of polishes made customarily for the purpose of cleansing as well as polishing is autombile polish, although it is also made in nonabrasive types.

Abrasive Liquid Automobile Polish. An abrasive polish in emulsion form suited to cleansing and polishing the painted surface as well as metal trim of an automobile is prepared from an oil and a wax, an organic solvent, water, abrasive, color, and an emulsifying agent to form a more or less permanent emulsion. Certain liquid polishes have softer waxes, petrolatum, or oil blended with a hard wax, such as carnauba, while others have all of the polish oil replaced with soft wax. The abrasive is necessarily a mild one such as tripoli. A small amount of bentonite is sometimes added to aid in the emulsification and to prevent caking or settling of the coloring pigment in the can. As a partial cleaner and as an emulsifier the triethanolamine (TE) salt of a fatty acid, e.g., triethanolamine stearate (TES), is used, although the trend seems to be towards the use of sulfonated hydrocarbon oils, e.g., petroleum sulfonates. Sulfonate of jojoba oil would be preferred were it freely available.

An automobile polish of the cleansing and polishing type which will leave a bright hard film is one prepared from *carnauba wax* 8, *ouricury wax* 2, *beeswax* 4, *petroleum ceresin* 3, petrolatum 0.5, high boiling naphtha 70, stearic acid 8, TE 3, water 80, and tripoli 55 parts. The waxes, stearic acid, and petrolatum are melted together and naphtha is slowly stirred in. The temperature is maintained at 90–95°C (nearly 200°F), and when the solution is clear the tripoli is added, and well mixed in. The water is boiled separately and added while hot with vigorous stirring so as to yield a good emulsion. The stirring is continued until the emulsion has cooled to room temperature; the polish is then ready for packaging.

A rubbing wax composition of the aqueous type can be made without the use of soft waxes, according to the specifications of Shapiro[148]. A solvent oil (b.p. 350–500°F, flash 140°F) is used to replace the softer waxes, thus securing a higher luster from the hard wax employed. The compound is formed by first mixing *carnauba wax* 143 parts, with solvent oil 300 parts, both heated to 190°F, or somewhat above the melting point of the wax. To this mixture 175 parts of air-flow tripoli are added with thorough agitation; and then oleic acid 55, and solvent oil 300 parts are introduced. During the entire process the mixture is kept at 190°F, and constantly agitated. Finally, triethanolamine (25) is separately dissolved in water (2300 parts) also kept at 190°F; this solution is intermixed with the general mass and continuously agitated while the balance of the water is added until the total water content has reached 8300 parts. Triethanolamine and oleic acid plus

the fatty acids of the wax act as emulsifying agents to stabilize the emulsion of oily water. The composition is agitated until the temperature drops to 65°F, when it is ready for filling containers.

Material which does not affect polishing or grinding, but serves to hold powdered or granular material together is known as a binding agent. In the above formulation, stearic acid and petroleum ceresin are the "binders"; the vegetable waxes the principal "hardeners"; petrolatum the "lubricating agent"; the *amino soap* (TES) formed by the chemical addition reaction of TE to part of the stearic acid the "emollient"; naphtha the "drier"; and tripoli the "abrasive." In a similar formulation of the paste type where about 25 parts of bentonite replace the tripoli, and are stirred into the finished emulsion instead of into the naphtha, the bentonite functions as a milder abrasive, but more particularly as an "adsorbing agent" for the liquid.

The polish is applied by rubbing over the surface well to remove dirt and streaks and then polishing with a dry cloth. In abrasive liquid and paste polishes, both liquid and paste, the abrasives are selected from the following: pumice powder, floated chalk, kieselguhr, koalin, and tripoli. Where soaps are used they must be of the soft kind, such as produced in the making of an emulsion of oleic acid, potassium carbonate, and ammonia water.

Abrasive Paste Automobile Polish. The paste type of polish is composed of a suitable blend of waxes and abrasives bound together by a solvent with a suitable water-emulsifying agent. A liquid polish is used as a one-step cleaning and polishing agent, whereas the paste product is sometimes used as a precleaner to a wax application from the nonabrasive liquid type of polish.

A water and abrasive type of polish has been described by Glickman[68] as prepared in three steps: (1) *carnauba, spermaceti*, and *ozocerite waxes* dissolved in naphtha; (2) diatomaceous silica, cream of tripoli, bentonite, color or dye, and water; (3) sodium borate, trisodium phosphate, soap chips of finest grade, and water. The waxes are heated and mixed with the solvent to yield a clear solution. The abrasive, bentonite, and color are mixed in warm water and stirred until free from lumps. The alkalies and soap chips are dissolved in boiling water. Then (2) and (3) are thoroughly mixed and the hot wax solution (1) is added to the mixture with sufficiently rapid agitation to insure emulsification. The product is then packed warm in suitable containers, glass or metal.

Nonabrasive Liquid Automobile Polish. This type of polish is prepared in much the same manner as the abrasive type, but with the abrasive left out. Many recipes are given in chemical formularies, in which oil, naphtha, wax or waxes, a mild detergent or emulsifying agent, and water are the components. One kind is prepared from castor oil, naphtha, alcohol, water,

potassium carbonate, spermaceti wax solution, light mineral oil, and chip soap. The spermaceti wax solution is prepared by dissolving 1½ pounds of spermaceti in a gallon of naphtha, and then filtering. This type of polish is followed by an application of a wax paste which contains a hard polishing wax.

Nonabrasive Paste Polish. In the manufacture of paste polishes of the nonabrasive type, the selected waxes are melted together. While stirring the wax base the mixed solvents are slowly added. For example, carnauba wax 18, and ozocerite 12, are melted and mixed with 70 parts of mineral solvent; or the 30 parts of wax base might contain 20 per cent of carnauba, 55 of candelilla, 5 of ozocerite, and 20 per cent of paraffine. The solvent might consist of 60 parts of naphtha, and 10 parts of kerosene, the latter to retard drying when the polish is applied; or a little turpentine and pine oil added to the mineral spirits. Utahwax has been used in place of ozocerite, for example, in the formula: carnauba wax 23, Utahwax bleached 34, paraffine (m. 130°F) 16, and naphtha 160 parts. In some of the softer pastes for automobile, floor, and furniture use, japanwax is utilized in conjunction with *carnauba wax*, *paraffine*, and *African beeswax*. Certain blends of synthetic resin with wax are said to be useful in improving the gloss and resistance to wear when used in the nonabrasive polishes.

Wax Spraying of Automobiles. Low-pressure wax spraying in the automobile polishing field represents a new advance in the art. Several spray waxes have made their appearance on the market, which have been rated by Moore[118] as good, fair, and poor. Waxes in solvents of a mineral spirits type are available for use in power sprayers and also are being sold in low-pressure aerosol cans. The ease with which spray wax can be applied to a cleaned automobile has a great appeal to both the professional waxer and the car owner. Cleaned cars can be wax sprayed with a power sprayer in about five minutes. It takes from ten to fifteen minutes with an aerosol can[118].

Formulations for spray waxes are based almost entirely on *carnauba wax*, or mixtures of carnauba wax, synthetic wax, and paraffine dissolved in light, volatile mineral solvents. In power spraying waxes, a range of 35 to 45 pounds per square inch of pressure is generally satisfactory. Aerosol can spraying is done at a slightly lower and less effective pressure.

Furniture Polish. Furniture polish at one time was confined to use in polishing wood furniture. Today it is used to polish both metal and wooden furniture, and differs principally from automobile polish in the absence of abrasives in its ingredients. Furniture polishes are largely nonabrasive liquid polishes, and almost invariably of the water-base formulation. In their preparation a mixture of the softer and harder, or polishing, waxes is preferred. Polishes suited for use with antique furniture should contain

amongst other ingredients, linseed oil, *beeswax*, and turpentine to give life to the wood, as well as a fair degree of luster. These polishes are more costly to prepare than the ordinary furniture polish for modern furniture.

In general the manufacturer employs an emusifying base, waxes, mild alkali, turpentine and/or naphtha, and water. Ordnance requirements as to fire hazard makes it necessary to have a polish so formulated that it will have a flash point of 105°F upwards. A polish patented by Shuger[152] comprises mineral spirits 169, light mineral oil 187.5, castor oil 93.6, ricinoleic acid 11, water 625, potassium hydroxide solution (1.65% strength) 19.2, and "Lanette Wax" 30 parts.

A polish of the emulsion type may be prepared from *carnauba wax* 8, *candelilla wax* 4, *beeswax* 4, *petroleum ceresin* 4, naphtha 70, morpholine 3, stearic acid 8, and water 180 parts. It is necessary to use a naphtha of high flash point. The waxes and stearic acid are melted in a hot water-jacketed kettle, electrostatically grounded for safety. The morpholine is added and then the naphtha very slowly until a clear solution is obtained at about 200°F. The water is brought to a boil and added to the naphtha solution and the whole stirred vigorously by an electrically operated (AC current) stirrer having a large-blade propellor with slow speed. After a good emulsion is obtained the stirring is continued until the product has cooled to room temperature. Morpholine emulsion films are said to become water-resistant within a few hours after application.

Polishes designed for use with light-colored woods are generally pale in color, and are also used to give luster to leather inlays, lacquer, bronze, plastics, painted, enamelled, and gilded surfaces. A liquid wax finish for wood can be made, according to Bryant[20], from kauri gum 20, *carnauba wax* 40, and stearic acid 31 parts, with seven times their combined weight of turpentine. A patented finish of similar kind consisted of kauri gum 20, *carnauba wax* 31, *beeswax* 18, stearic acid 31, and turpentine 700 parts.

Old English Tinted Furniture Wax. Polishes in paste form are made up with wood stains or tints for use on different woods. To illustrate, a "maple tint" is used on Colonial, bleached walnut, bleached mahogany, cherry, beech, ash, golden oak, satinwood, pine, honey maple, etc. A "walnut tint" is used on the different kinds of walnut, Tudor oak, and Feudal oak furniture. A "mahogany tint" is used on the various mahoganies. The object of a tinted finishing wax is to tone down unsightly scratches and nicks in furniture without changing the color of the finish itself. It should also produce a brilliant polish with a light touch of the polishing cloth. The wax foundation generally consists of such waxes as *carnauba*, *esparto*, and *beeswax*.

The sale of furniture polishes in food stores in the United States in 1950 amounted to $10,894,000, exceeded by the sale of auto polish $18,298,000,

and shoe polishes (other than white) of $22,395,000. About 850,000 pounds of carnauba wax per annum are consumed in the manufacture of furniture polishes, and an equivalent amount of other hard waxes divided between *candelilla*, *ouricury*, *sugarcane*, *beeswax*, *montan*, and *special synthetic waxes*.

Flash and Fire Points of Solvents. Municipal ordinances often require that the flash and fire points of furniture or other polish attain a specified minimum, for example 105°F. The addition of high boiling naphtha to turpentine is an example of how the flash and fire points may be elevated to come within the specified requirement.

Mixtures of spirits of turpentine and naphtha ("Bayol D") gave flash and fire points as tabulated below.

Percentage of "Bayol D"	Flash Point (°F)	Fire Point (°F)
0	94.5	96
10	98	98
15	99	100
20	101	102
25	103	105
30	108	108
40	109	110
45	110	111

Mixtures of spirits of turpentine and carbon tetrachloride (CCl_4) gave flash and fire points as tabulated below.

Percentage of CCl_4	Flash Point (°F)	Fire Point (°F)
0	94.5	96
5	100.5	103.5
10	114	117
15	126	130.5
20	132	137
25	144	148.5
35	154	157

Mixtures of naphtha ("Varnolene") and carbon tetrachloride gave the flash and fire points as tabulated below.

Percentage CCl_4	Flash Point (°F)	Fire Point (°F)
0	106	108
5	117	120
10	126	130
15	143	146
20	150	152
25	164	166
35	176	177

Mixtures of xylene and carbon tetrachloride gave flash and fire points as tabulated below.

Percentage CCl_4	Flash Point (°F)	Fire Point (°F)
0	86	90
5	96	100
10	107	111
15	114	122
20	137	139
25	142	144
35	184	202

Mixtures of (a) toluene, or (b) "Benzo-Sol," or (c) with carbon tetrachloride gave flash and fire points as given below.

Percentage CCl_4	Toluene		"Benzo Sol"		Acetone	
	Flash	Fire	Flash	Fire	Flash	Fire
0	below 77°F	below 77°F	below 77°F	below 77°F	below 77°F	below 77°F
15	77	85	—	—	—	—
20	80	90	—	—	—	—
30	—	—	below 77	below 77	below 77	below 77

Flash and fire points of furniture polishes are as follows:

Sample	Flash Point (°F)	Fire Point (°F)
A	105.8	109.4
B	163.4	—
C	84.2	91.4
D	104	109.4

Solvents of Naphtha Type. Hydrocarbon solvents of the mineral spirits group comprise mineral spirits, V. M. & P. naphthas, rubber solvents, and narrow range solvents. Generally speaking the aliphatic solvents are spoken of as naphthas. A naphtha such as "Varsol" (Esso Standard Oil Company) has a boiling point range of 300 to 400°F, whereas V. M. & P. naphtha has a fast drying rate, and ranges from 250 to 290°F in boiling point. A slow drying, higher flash naphtha is produced with a boiling point range of 325–470°F. Examples of close cut solvents are "Esso Solvent No. 7," which has a range of 250–290°F, and "Esso Process Naphtha" with a range of 200–210°F. Much lower boiling solvents of close cut are produced for extraction purposes, for example, hexane (b.pt. 160° ± 6–10°F) used in the extraction of cacao butter as well as the oil from soybeans, rice hulls, castor beans, etc. It contains some heptane and octane. Another narrow range low boiling solvent is heptane (b.pt. 210°F). Rubber solvents have ranges such as 130–250°, 140–240°, and 160–290°F. *White spirits* is the English term for mineral spirits.

Liquid Stove Polish. A stove polish generally consists of a water dispersion of graphite, a black pigment, wax, resin, and a suitable emulsifying agent. The usual procedure in making liquid stove polish is to melt the waxes together with oil-soluble nigrosine, then thin out with turpentine, and mill in the graphite and lampblack. Graphite is the foundation ingredient which cannot be readily burnt off, whereas the lampblack deepens the color, but burns off readily. The polish must be well rubbed with a soft brush to give a good luster.

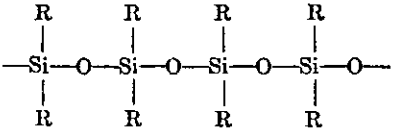
A formula given by a manufacturer of *diglycol stearate* for a liquid stove polish is the following: *montan wax crude* 5, rosin 1.5, *paraffin wax* (m. 40–42°C) 2.5, *diglycol stearate* 2.5, potassium carbonate 3.5, graphite 50, boneblack 20, nigrosine oil-soluble 3, turpentine (or substitute) 97, and water 115 parts by weight. Coumarone resin may be used in place of rosin.

Colloidal clay is sometimes used with the blacks to prevent the polish from caking. *Ozocerite, petroleum ceresin,* and *carnauba waxes* are also sometimes used in stove polishes. What is commonly called "stove blacking" is simply a mixture of graphite, lampblack, rosin, and turpentine, and contains no wax.

Silicones in Wax Polishes. Not more than a mere fraction of silicone oil can be incorporated in waxes. Because of the incompatibility of the silicone oils in waxes, the silicone oil must be used with the wax in a mutual solvent such as mineral spirits (b.p. 275–325°F). The wax and silicone are mixed with about 20 per cent of the total solvent, which constitutes 90 to 95 per cent of the polish, by heating to 190–200°F. When the solution is complete, the remaining solvent (at about 120°F) is added with agitation. The mixture is cooled with agitation and the agitation continued during packaging to prevent settling.

Silicones produce a high degree of slip in polishes without causing the wax to smear, and find an extensive use in no-rub automobile and furniture polishes. With the precleaned surface the polish is spread smoothly, allowed to dry to a powdery film, and the film wiped off leaving a high gloss with no rubbing.

Silicone oils have the following basic structure:



R may be methyl, ethyl, phenyl groups as such or in combination. Dimethyl and diethyl silicone oils are sometimes preferred because of suitable viscosities; this is particularly true of the dimethyl oil. Silicone furniture polishes have also been prepared from silicones which are trialkyl deriva-

tives of silicon halides, e.g. trimethylfluorsilane, Me_3SiF (b.p. 16.4°C, f.p. −74.5°C) or dialkyl mixed halosilane e.g. dimethyl chlorofluorsilane, $Me_2S{:}ClF$ (b.p. 38.4°F, f.p. −85.1°C), etc. Only a small fraction of one per cent of these select silicones are used in the polishes. These silicone oils have no softening effect on the wax, and make it easier to spread, bleeding to the surface to give added protection. The wax used in preparing a silicone polish is usually an oxidized microcrystalline (OMC) wax. The silicone oils commonly used are either the methyl or ethyl oils.

A no-rub automobile polish known as "Car Polish 4G" is of the silicone–wax–solvent type, and is comprised of silicone oil 1.5, OMC 2.5, and naphthol mineral spirits 96 parts. A furniture polish may be prepared from silicone oil 2.2, OMC 3.6, and mineral spirits 94.2 parts. According to Welch[1716] the great ease and speed with which such polishes can be applied for highly finished furniture has favored their general use.

The Petrolite Corporation, New York, has published a water emulsion type of silicone no-rub furniture polish which is comprised of OMC wax ("Crown Wax 23") 3, silicone (5000 cs visc.) 3.6, oleic acid 3.6, morpholine 1.7, mineral spirits 67.5, and water 40.0 parts. The wax, silicone, and oleic acid are dissolved in the mineral spirits, and an emulsion formed, the customary wax to water of the water to wax technique.

A "wax-silicone cleaner" can be formulated from silicone oil 2, OMC wax 1.7, oleic acid 2, "Varnolene" 36, morpholine 0.8, diatomaceous silica 10, air-floated clay 2.5, and water 45 parts. The first three ingredients are brought into solution in hot mineral spirits; the last four ingredients are stirred together and brought to the same temperature. The solvent solution is added to the slurry with high-speed agitation; this results in a very fine emulsion with abrasive properly suspended.

Shortly after the application of the silicone polish to a table top, or when it becomes dry, it can be easily rubbed without pressure to a high luster with a soft cloth. The polished surface, because of the excellent release characteristics of silicones, does not collect dust. Silicone polishes are also useful for polishing chrome, porcelain, leather, etc., as well as wood. A brighter gloss is obtained with methyl silicone oil, but a deeper, richer gloss with ethyl oils.

Buffing Compound. Various items of metal are finished with the aid of abrasive compositions; the operations of finishing are generally known as polishing, buffing, and lapping, and are conducted with the abrasive applied to a flexible polishing wheel or an endless belt. In buffing, a smaller size of abrasive is generally employed than for polishing. No adhesive is used to carry the abrasive grain on buffing sheel. The abrasive is fed to the wheel by means of buffing sticks, made up in various compositions. Buffing compositions often carry a hard grease or *beeswax*.

A polishing composition suitable for buffing sticks is given by Libovitz, *et al.*[106]. The composition has sufficient tensile strength to hold together under stringent conditions of use and yet is soft enough to be applied to the surface of the buffer wheel. It is also claimed to polish hard surfaces like steel without undue wear and tear of the buffer wheels used during the polishing operation, and will hold the buffing wheel firm. An example of the polishing compound described consists of silicous earth 1250, petroleum jelly 250, *ceresin wax* 150, *stearic acid* 50, *montan wax* 50, tar 25–250, and cotton waste 25–250 parts by weight.

Buffing of copper surfaces employs fine and relatively soft abrasives, such as red or purple ferric oxide, tripoli, or lime, with a wheel of wool felt. The buffing compound is prepared by mixing the abrasive with *stearic acid* and tallow, and forming it into bar, cake, or stick which is pressed against the revolving felt wheel.

Application of a Finishing Wax. In applying wax to floors, linoleum, furniture, and woodwork, certain directions must be followed. All surfaces to be waxed must be free from dust, dirt, grease, etc. Apply a thin, even coat of the wax paste. This can be done conveniently by placing a small quantity of the wax in a double thickness of cheese cloth; apply only the amount which works through the cloth as it is rubbed over the surface, assuring even distribution. Allow the surface to stand until dry (usually 10–15 minutes) and polish with clean rags, a weighted brush, or an electric polisher.

Manufacturers of certain plastic objects polish the pieces with a hard wax in revolving drums equipped with stout wooden pegs fastened to the inside; the pegs are coated with the wax before insertion into the holders. The objects are waxed to a polish by being continually rubbed against the waxed pegs. The number and size of the pegs is regulated according to the sizes of the objects polished.

Metal Polishes. Metal polishes are manufactured and marketed in several different forms, such as cake, powder, paste, or liquid. Certain types are of general utility for polishing many kinds of metal, whereas others are made for specific uses, such as brass polish, silver polish, aluminum polish, etc. A liquid polish known as "Glass Wax" is used for silverware, brass, copper, aluminum, and chrome finishes.

Most of the metal polishes carry light abrading material such as silica, whiting, calcined kieselguhr, tripoli powder, levigated alumina, etc. Liquid metal polishes may be formulated from *carnauba wax*, *candelilla wax*, stearic acid, linseed oil, abrading material, water, and triethanolamine. Organic solvents are included to help dissolve grease and speed drying. For example, wax 5, triethanolamine soap 2, naphtha 15, diatomaceous earth 15, and water 73 parts.

A metal polish of the paste type was prepared by Pease and McDonnell[180] according to the formulation: *carnauba wax* 1 lb, stearic acid 1 lb, ammonium hydroxide 3 oz, paraffin oil 9 pints, and abrading material (e.g., "Silex") 29 lb.

Glass Wax Cleaners. A glass wax cleaner is used as a cleaner and polish for glass. A product with the trade name "Glass Wax," Gold Seal Company, Bismarck, North Dakota, requires that a small amount of the liquid be poured on a damp-dry cellulose sponge (for glass) or soft dry cloth (for metals), whence it is applied in a light coat to a dry surface, and when dry is wiped off with a soft clean cloth.

Glass wax cleaners contain fine, grit-free diatomaceous earth as the abrasive and bentonite as a suspending agent. The liquid portion generally is comprised of an *organic solvent*, the purpose of which is to help dissolve grease and speed drying; an *emulsifying agent*; *ammonia*, as an adjunct cleaning agent and to impart a refreshing odor; and *water*. One formula proposed for a glass wax cleaner includes bentonite, isopropyl alcohol, carbon tetrachloride, naphtha and propylene glycol monoöleate, and water. Some glass cleaners contain silicone, which remains as a film on the glass; the film is said to protect against fogging and to keep grime from fixing itself on the glass. Although a glass wax cleaner may contain a very small amount of wax (e.g., "Carbowax"), it is uncertain that wax of any kind as a component is essential for the cleaner to function properly.

WAX USED IN PRINTING PROCESSES AND PRINTING INKS

Electrotype Impressions. When it is desirable to produce several plates from the original type or linotype slugs, a process known as electrotyping is employed. In the electrotyping process, as in stereotyping, an impression of the surface is made, using wax as a medium, although resinous compositions and lead also are utilized. For the wax the most suitable medium is *ozocerite*. In the absence of European ozocerite, both South American and Utah ozocerites have been successfully used. *Beeswax* is also used for the purpose and may be admixed with the oxocerite. The impressed mold is made conductive by a coating of graphite. The wax and resinous molds are then treated with aqueous copper sulfate and iron to form a thin coating of copper on the mold. Subsequently a layer of copper is deposited upon the surface electrolytically, resulting in a metallic sheet whose surface corresponds to that of the type from which the impression was taken.

Electrotypers' Waxes. Electrotyping comprises a process of duplicating printed matter and designs by depositing electrolytically a metal or mixture of metals from solution onto a design-impressed body of wax which has been rendered electrolytically conductive. When the deposition is complete the wax is stripped off, and the deposited electrotype is ready for the print-

ing machine. By such a procedure several plates can be produced from the original type or linotype slugs. Woodcuts, medals, and other objects are also reproduced by electrotyping.

In the electrotyping process, as in stereotyping, an impression of the surface is made, using wax as a medium, although resinous composition and lead also are utilized. The most suitable wax medium is *ozocerite*. In the absence of European ozocerite, both South American and Utah ozocerites have been successfully used. *Beeswax* is also used for the purpose and may be admixed with the ozocerite. The impressed mold is made conductive by a coating of graphite. The wax and resinous molds are then treated with aqueous copper sulfate and iron to form a thin coating of copper on the mold. Subsequently a layer of copper is deposited upon the surface electrolytically, resulting in a metallic sheet whose surface corresponds to that of the type from which the impression was taken.

An "electrotypers' wax" may be prepared from (a) *ozocerite* 63.5, *beeswax* 31.7, graphite 4.8 parts; or (b) *beeswax* 85, burgundy pitch 5, turpentine 10, *ozocerite* 95, and graphite 5 parts. Electrotypers' wax is melted and poured upon the metal plate in a layer ¼ inch thick and is then smoothed off with a tool and a torch. The plate is placed upon a table heated by steam or electrically to keep the wax soft until the cold wax-engraved plate is superimposed face down upon it. The combined plates are then clamped together in frames and when wax engravers' plate is removed, the design will have been impressed into the wax for electrotyping.

Engraver's Wax. Engraver's wax is prepared from *beeswax, paraffin wax*, a resinous pitch, rosin, and zinc oxide. The waxes and gums are melted first in a shallow open container and then the powdered zinc oxide is added with slow and continual stirring. Examples of formulations are (a) *white wax* 40, *yellow wax* 8.9, *paraffin wax* 26.7, burgundy pitch 6.7, rosin W W 4.4, and zinc oxide 13.3 parts; (b) *white wax* 4.5, *yellow wax* 1.0, *paraffin wax* 3.0 burgundy pitch 0.7, rosin 0.5, and zinc oxide 1.5 parts. The final mixture should contain free ZnO, zinc salts of fatty acids, inert paraffin, and esters of beeswax. Burgundy pitch is a rosin from the Norway spruce tree. The wax engraver pours the warm mixture onto the upper surface of the plate in a layer about ⅛ inch thick, and after waiting for it to harden or congeal he smooths off the surface with a special tool to give uniform thickness and proceeds to cut the design.

Printing Inks. For convenience printing inks may be divided into classes: (1) typographic, (2) lithographic, (3) intaglio. Typographic printing or letterpress printing includes all the processes of printing from raised characters or plates. Lithography or offset printing is the printing from a slightly etched stone, or other suitable medium. Since the printing from flat surfaces has been extended to slightly etched metal plates, the term

"planographic" is now used to cover offset lithography, dry offset printing, and offset tin printing, as well as stone lithography. Gravure or intaglio printing may be defined as the process of printing from engraved surfaces, such as engraved copper or steel plates. Modern gravure printing is done principally from cylinders, or web presses, and is generally referred to as rotogravure. Waxes are used in the "ink compounds" added to inks to modify their working properties. Waxes are often instrumental in producing films which exhibit a certain "slip" and are "scuff resistant." Most commonly used in printing inks are the petroleum waxes, both paraffin and microcrystalline. Nonmineral waxes such as carnauba and candelilla, as well as synthetic waxes such as polyethylene wax, are used in small quantities in many inks.

Systems of drying ink films are (a) drying by absorption, (b) drying by gelation, (c) solvent evaporation, (d) drying by precipitation, (e) cold set process. The term "oxidative-polymerization" is drying by a combination of oxidation and polymerization; the carrier liquid is generally a processed linseed oil.

Typographic Inks (Ordinary). Typographic inks are used for newspapers and magazines, and most often are black in color. High-quality inks for depressed surface plates (intaglio printing) are preferable for advertising displays and for rotogravure processes. Carbon black has great tinting power and makes excellent typographic ink of fine working quality. By a proper combination of varnish and carbon black, the desired effect in typographical printing-ink can be achieved. Carbon black takes 82 per cent and lampblack 72 per cent of varnish oil to grind the pigment into paste form. The ink with the lampblack tends to be "short," of poor flow, and grayish overtone.

It occasionally becomes necessary to modify the properties of typographic inks by the addition of compounds. Such ink compounds comprise one or more combining materials consisting of inexpensive waxes, soaps, greases, and oils. The purpose of an ink compound is to improve the working and setting quality of the ink, and to eliminate such troubles as offsetting, sticking, and picking. *Crude montan wax* is extensively used as a compound ingredient since the wax is hard, works well, and aids in the setting quality of the ink. The action of compounds seems to be mainly colloidal in nature in that they tend to break the gel formation of the varnishes by reducing their cohesion and adhesion. They also act as emulsifying and dispersing agents, tending to prevent flocculation or agglomeration of the pigment particles. Common hard soap has been used in inks but has fallen in disfavor because of the difficulty of properly incorporating it in the inks. Grease, such as soap suspended in mineral oil, is easily incorporated in an ink, but is apt to leave a stain on the paper or on the hands of the reader.

Typographic Inks (Superior). The addition of waxes, such as *beeswax, ouricury wax, etc.*, improves the quality of the ink but increases its cost. However, a considerable amount of such waxes is used in compounding high quality typographical printing inks. *Woolwax*, or *anhydrous lanolin*, is a suitable compounding material since it is emulsifiable and readily dissolved by naphtha and other common solvents. When added to ink it makes the ink "long" and it tends to improve the lifting and working qualities of an ink which is otherwise "short," also of an ink which has pigments of low oil absorption or high specific gravity. Its principal use, however, is in its combination with either paraffin or beeswax as a noncrystallizing compound for use in first color, opaque, process yellows. *Woolwax* has the power to hold small quantities of *paraffine* or *beeswax* in suspension, thus preventing them from crystallizing out of the inks and causing an undesirable graininess. The paraffine or beeswax should be melted with the woolwax or wool grease, cooled, and then given a run over the mill before the compound is introduced into the ink. Tallow is also sometimes used in printing inks.

The rapid printing of the McKee four-color machines made it necessary to devise a method for quickly drying the sheets to prevent offset or smudge. This was first accomplished by interleaving the freshly printed sheets with specially prepared manila paper; and later by spraying of a coat of powdered paraffin over the printed surface. Since the introduction of infrared ray lamps to dry the ink on the printed surface, it is essential that the fluid ink is of a composition which will set rapidly. A rapid setting of the ink may be brought about by the introduction of a high melting hard luster-producing wax, such as *polyethylene wax* preferably blended with 10 per cent (more or less) of *anhydrous lanolin*.

Beeswax is a common ingredient of nonoffsetting and noncrystallizing compounds. According to Wolfe[176] it produces a somewhat less grainy compound in general than does paraffin wax, and possesses better working and gripping qualities. The incorporation of from one-half to one ounce of beeswax to the pound of ink by melting and grinding will enable the ink to be printed on top of a crystallized color without crawling. The inclusion of a little *lead oleate* or paste drier along with the beeswax will increase the grip of the ink on the dried surface and improve its drying quality. Beeswax facilitates clean printing on an "offset" printing press.

Paraffin wax is customarily employed in conjunction with a nonpetroleum wax by the ink maker, since if used alone it is apt to crystallize out. Paraffin is, however, occasionally used as an adjunct to petrolatum, and without the addition of another wax.

Montan wax has found a constantly increasing field of application as a substitute for *carnauba wax* in the preparation of ink compounds. Wolfe[176] states that it is possible to incorporate more of it into a given ink than

carnauba. *American montan wax*, which is somewhat dark in color, has proved a valuable ingredient of printing inks which are dark in color, such as black, brown, blue, etc.

Carnauba wax is occasionally used in ink compounds for bronzes, etc. The use of carnauba wax in a bronze printing ink is described in the following recipe by Mason: polymerized tung oil (240–280°C) 37, linseed oil (boiled) 19, carnauba wax (refined) 4, turpentine (spirits) 7, and bronze powder 33 parts. In the formulation of the bronze ink the boiled linseed oil is added to the polymerized tung oil and the mixture is kept at 200°C for two hours, during which time the wax can be melted in and dispersed by stirring. After cooling, the bronze powder is moistened with the turpentine and stirred in before milling for smoothness and uniformity.

Ozocerite is superior to paraffin for use in printing inks since it will not crystallize, and the addition of 25 per cent or more of ozocerite to paraffin will prevent paraffin from crystallizing. Ozocerite is, however, an expensive wax to use. In general it retards the drying of inks and reduces their stack.

Petroleum ceresin waxes such as petroleum *ozokerite* and the *"Aristowaxes"* have a similar field to the imported ozocerite in printing inks and are also less expensive to use.

Petrolatum itself finds a wide application as a reducer, extender, and cheapener in the manufacture of colored perfecting press, poster, and show card inks. A white ink for printing cellulose and cellophane is made from titanium oxide 63, long oil varnish 6, lithographic oil 29, and paraffine in petrolatum 2 parts. The latter is made by melting 6 parts of paraffine in 94 parts of *petrolatum*. The varnish is made by heating 10 parts of alkyd resin with 750 parts of tung oil for an hour. The ink is said to adhere to cellophane and be tack-free in four hours.

Other waxes which go into the manufacture of varnishes, paints, and printing inks include *sugarcane wax*, special synthetic waxes as *"A-C Polyethylene #6,"* and hydrogenated castor oil waxes as *"Castorwax."*

Somewhat over 500 million pounds of printing inks are being produced in the United States, a very large proportion of which contains no wax ingredients. The total amount of waxes used by the ink maker inclusive of petrolatum is believed to approach 3,000,000 pounds per annum. The total amount of the hard waxes consumed is somewhat less than 1,000,000 pounds of which amount the synthetic waxes constitute a substantial proportion. Commercial fatty acid amides (see "Armids," p. 482) are effective anti-offset, antiscratch agents for use in printing inks. Unlike most such agents, they allow overprinting by another color.

Process Inks (Typographic). By properly combining, or superimposing, the three so-called primary colors, red, yellow, and blue, practically any color may be reproduced. This is the fundamental principle upon which

three-color process printing is based. Halftone plates are made from negatives of pictures taken with a camera using color filters. The manufacturer of process inks requires closer control of the physical characteristics than any other type of printing ink. The second color should be less tacky than the first color, and the third color less tacky than the second. Wolfe[176] gives the following recipes for the process inks:

Process Transparent Yellow No. 00 transparent litho varnish 25, No. 1 transparent litho varnish 15, soft wax compound 6, paste drier 4, quinoline yellow lake on hydrate base, dry 50 parts by weight.

Process Blue. No. 00 transparent litho varnish 36, No. 1 transparent litho varnish 11, cobalt drier 6, soft wax compound 5, phosphotungstated Victoria blue toner, dry 1, Peacock blue lake on hydrate base, dry 41 parts.

Process Red. No. 00 transparent litho varnish 36, No. 1 transparent varnish 15, soft wax compound 5, paste drier 5, phloxine toner, dry 25; aluminum toner, dry 25; aluminum hydrate, dry 30 parts. The soft wax compound can be made with *anhydrous lanolin*, in combination with *paraffine* or *beeswax*. The compound ingredients are melted together, cooled, and then given a run over the mill before the compound is introduced into the ink. Wool grease, or anhydrous lanolin, is especially valuable in inks that contain considerable proportions of pigments of low oil absorption or high specific gravity (e.g., chrome yellows) as it tends to improve their lifting and working qualities.

Lithographic Inks. A small percentage of tallow and *wax compound* is often added to lithographic inks to make them more water repellent so that they will resist the action of the dampening solutions more completely. The compound also aids the working of the ink by slightly reducing the tack. Two per cent of the usual compound is ordinarily sufficient for this purpose. In offset lithographic printing the waterproof ink is transferred by a dampened roll to the etched metal plate and from there to a revolving cylinder covered with a rubber blanket and thus onto the sheet to be printed, e.g. paper or tin plate. Waxes are only occasionally used in the offset T.P. (tin printing) inks. *Wool grease*, however, is used in dry offset printing inks for printing tinted backgrounds for checks, labels, etc. A little wax compound added to the ink improves its working qualities. Dry offset inks need not be waterproof. *Japanwax* may be used in dry offset inks.

A typical lithographing ink for paperboard in which ink *woolwax* is used, comprises: *woolwax* 2, spindle oil 1, heavy lubricating oil 42, water 45, carbon black 8, induline 0.8, and red oil 1.2 parts. The spindle oil is warmed with the woolwax; the induline is ground with the red oil. The woolwax solution is mixed with the lubricating oil and water added next. When smoothly emulsified the carbon black and ground color are stirred in and the mixture is milled.

Intaglio Printing Inks. Under this heading are many kinds of ink for (a) copper plate engraving, (b) steel plate engraving, (c) stamping, (d)

photogravure, (e) rotary photogravure, (f) thermographic processes. Waxes are seldom used in the intaglio printing inks, except in the so-called "transfer inks," which are used on the base paper material prior to printing the design.

Transfer Inks. In intaglio printing, certain types of waxes have been employed in treating temporary transfer bases prior to printing of the design. Wade[163] impregnated a sheet of thin paper with paraffine for pressure transfer and the pattern was placed on the wax with ink containing a nondrying oil (castor). Foundation materials for transfer inks may include rosin with the wax. The rosin is sometimes substituted for by paracoumarone, e.g., a composite of Chinese insect wax and paracoumarone can be used to coat glassine paper, and a design effectively placed on this with a nitrocellulose metallic powder marking compound. Shellac sizing is subsequently added to the print. For some purposes, instead of printing the design on a wax coating, the pattern is stamped out from a cellulose ester film, and attached to the waxed surface by means of gum damar or other suitable adhesive.

Wax-set Inks. Wax-set inks are most often inks which contain no wax but the binder of the ink precipitates to form a hard protective film when the printed surface is immersed in wax. This is accomplished by making the ink from pigments and "wax-set vehicles" which customarily are solutions of nitrocellulose or alkyd resin in a high-boiling solvent. The wax-set inks are used for printing bread wrappers, milk bottle caps, etc.

Gravure Printing Thermo-fluid Inks. For large volume high speed printing by gravure, letterpress, or offset, of containers, publications, and literature of all sorts, Huber[87] invented a type of printing ink which is normally solid but which becomes fluid when used with a heated letterpress, litho and/or gravure printing machine. The ink is heated to an elevated temperature at which it is molten and possesses a suitable printing consistency. A printing effect is obtained in which there is no penetration to the fibers. An example of a composition of the fusible ink is given by Huber as carbon black 10, gilsonite 45, *candelilla wax* 45 parts. The wax is first melted and the carbon black thoroughly incorporated into the wax by use of mixing and milling equipment, after which the gilsonite may be added in a steam-jacketed mixer. The ink softens at about 64°C, and prints well at 75°C. A more complex composition is given as gilsonite 50, *candelilla wax* 40, chrome orange 6, No. 3 litho varnish 3, and carbon black 1 parts. Blends of *candelilla wax* and gilsonite have the property of wetting and adhering to the fiber of the stock. Another sample is "Santo Resin" 60, *ozocerite* 20, and peacock blue 20 parts. "Santo Resin" is the isobutylene polymer of the Monsanto Chemical Company. It melts at 104°C. A rotary letterpress ink suitable for the printing of magazines is as follows: "Cumar V" 20, carbon black

9, and toners 2 parts. This ink melts at 78°C, is liquid at 85°C, and has a suitable printing consistency at about 100°C.

In the gravure printing with thermo-fluid inks the etched plates do not require deeply etched cells, and the etchings are best made up shallower than customary for the wet inks. The press is equipped with suitable heating means to maintain the ink in a proper liquid condition during the printing operation.

Heat-Set Inks: A heat-set ink, whether embodying a pigment or dye, depending upon the particular type of printing to be done and the characteristics desired, may be admixed with any or all of various materials commonly used in the manufacture of printing inks such as toners, extenders, fillers, wetting agents, *waxes*, compounds, thinners or reducers, and driers, properly dispersed in a vehicle. Seil and Cole[147a] proposed a vehicle consisting of 2 parts by weight of partially polymerized resin dissolved in about 1 part of aliphatic hydrocarbon solvent (b. 500–600°F) substantially nonvolatile at room temperature. The partially polymerized resin can be made by reacting phthalic anhydride 81, glycerine 64, and soybean fatty acid 81 parts. The resultant vehicle, although it contains 65 per cent or more of solid matter and only 35 per cent or less of solvent, nevertheless has the required low viscosity for a printing ink vehicle.

By reason of its high solid content the heat-set ink can be laid down upon the paper in multi or process color printing in one pass through an appropriate press, without the necessity for drying each color application before applying the succeeding one. The gas heating equipment at the delivery end of the press hardens, sets, or polymerizes the vehicle of the ink, whether applied in single or multiple impressions. Sheets delivered from the press at the rate of even 5000 or more per hour may thus be directly stacked upon each other without danger of offsetting, smudging, sticking, or picking, with the elimination of slip sheeting, spraying, racking, traying, or other expensive expedients intended to mitigate those evils[147a].

In heat-set inks a vehicle of the type described permits the use of color base dyes, such as nigrosine, rhodamine, Victoria blue, malachite green, and diazaphane yellow base. The recent incorporation of polyethylene wax in heat-set inks permits faster hardening and setting without interference of the polymerization of the vehicle by the gas heating equipment. It also allows the use of a greater proportion of ester gum to alkyd resin, thus reducing cost of the ink, without causing the ink to remain sticky on the sheet.

Steam-set inks used in typographing or letterpress printing of paperboard material which is to be fabricated into cartons, etc., are prepared with pigments and vehicles in which *polyethylene wax* is an ingredient. The use of the polyethylene wax not only permits faster setting, thereby allowing a

much speedier output of the printed paperboard, but aids in giving brighter and more glossy colors.

Cold-set Inks. Cold-set inks are made to be printed at temperatures above their melting point and solidify at the delivery end of the printed sheet material. They differ from heat-set inks which require gas heating at the delivery end to set or polymerize the vehicle of the ink. The cold-set process has been of limited value commercially because of difficulties encountered in the mechanics of operation. The cold-set inks are usually printed at 221–230°F and are made to solidify at 167–176°F. Cold-set ink vehicles are a mixture of resins, waxes, pitches, plasticizers, or similar materials. The inks have some decided advantages aside from the speed of printing, namely lack of penetration, yet excellent adhesion and elimination of transparency. The type of reproduction is remarkably sharp and the halftones are excellent, even on rough paper. The use of polyethylene wax in cold-set inks lends to the smoothness of printing at the higher temperature and aids in the solidification of the ink at the delivery end of the press.

SEALING WAX

Historical. The wax seals used in medieval times were made from resins and *beeswax*. Analyses by Dobbie and Fox of ten seals dating from 1306 to 1504 revealed that all were of this composition. The only deleterious effect of time on these waxes appeared to be a slight absorption of oxygen. The coloring matters used in these seals were found to be verdigris and vermilion. [Dobbie, J. J. and Fox, J. J., *J. Chem. Soc.*, **105**, 795–800 (1914)].

The modern sealing wax cannot with truth be called a wax, because it is essentially a mixture of resins, turpentines, neutral material for bulking, pigments, and volatile balsams and essential oils. The mass is melted and formed into sticks. The origin of the term "sealing wax" is an ancient one, dating back to the time when colored beeswax was used for sealing letters, and for attaching the impression of seals to documents. Many centuries ago when lac from the East Indies was introduced in Venice the use of beeswax in making sealing wax came into discard. In Spain the lac became known as "Spanish wax" only because of its use in making sealing wax. Gummed envelopes greatly lessened the common use of sealing wax in correspondence and its use in sealing registered mail is no longer permitted by U. S. Post Office regulations.

Kinds of Sealing Wax. Standage[156] attempted a classification of sealing waxes into "extra superfine," "superfine," "fine," and "common," according to the grades of material used. Parcel wax, used for spreading over the strings of packages, is of a lower grade, and is made of cheap color such as minium, and common rosin. Recently, sealing waxes have been made in the form of a candle, with a wick, so that a special source of

heat for melting the wax is not needed. In these candles the wick is imbedded in paraffin wax, and separated thus from the sealing wax, composition, as described by Aktiebolaget Lackyljus[7]. Or, the wick in the center of the stick, usually of from 8 to 12 cotton threads, will have been impregnated with stearine. It is held taut in the forms while the molten wax solidifies around it during the cooling. Sealing waxes are also made for the bottling trade.

Ingredients of Sealing Waxes. Gum lac, mastic, sandarac, and benzoin are used with turpentine in some of the superfine qualities of sealing wax. The resin mostly used is bleached shellac or orange shellac, and the turpentine genuine Venetian. Perfumed sealing waxes have essential oils and balsams added. Some of the perfuming materials used are pinene, Peruvian balsam, mastic, and musk. An addition of 2 per cent of benzoin and 1 per cent of Peruvian balsam, imparts a very agreeable odor to sealing wax. The perfume can be much varied by an admixture of small quantities of oil of peppermint, or bitter oil of almonds. The bulking bodies are chalk, gypsum, baryta, zinc white, etc. The pigments include various reds, yellows, blues, greens, browns, or blacks. In the finer qualities of sealing wax on the market, the best pale shellac is most often the chief ingredient, while genuine Venice turpentine, and/or balsams Peru and tolu, magnesia, and a high-quality colored pigment form the other constituents. In the lower grades rosin is dissolved in artificial turpentine, and the pigment incorporated. The pigment may be chalk, soot, Indian red, ocher, or other earth.

Manufacturing Procedure. First, the shellacs or resins are melted in an enamel-lined cast iron pot, and while stirring with a flat wooden paddle, the turpentine, previously heated and strained, is added. Then follows the addition of the neutral fillers and the pigment, with continued stirring to ensure intimate mixing. There are instances where the color must be premixed with the filler and gum spirits of turpentine to secure the proper tint, the mixture warmed, and then added to the molten mass. Aromatic substances are added last. The molding of sealing wax is done in "forms" made of brass or bronze. The wax is customarily molded into triangular, square, or rectangular sticks. The form may consist of a rectangular brass plate into which are cut appropiately shaped grooves, for example, a "v" shaped groove for triangular sticks, or a channel with three equal sides for square sticks. A double mold must be used for round or oval sticks. The wax is ladled from the casting spoon into "form" plates previously warmed. The sticks are then gradually cooled and after turning them out of their grooves must be polished and dressed. The polishing is done by hand on a hot plate, and the maker's imprint is impressed on the sticks from a brass die, the sticks being patted by wooden pallets to keep them in their cast shape.

Colored Sealing Waxes. In the preparation of a black sealing wax the finer qualities are made with Venice turpentine and shellac in about equal or somewhat greater proportion, and lampblack or ivory black mixed in turpentine is added as the pigment. The ordinary black sealing wax is made with shellac, rosin, turpentine, whiting, and lampblack or boneblack. A deep blue sealing wax may be made from 2½ parts of shellac, 1 of Venice turpentine, ⅓ of white rosin, and ⅓ of mineral blue. A very light blue sealing wax may be made from 15 parts of bleached shellac, 35 of gum mastic, 50 of turpentine, 35 of calcined mica, and 25 parts of ultramarine. A very dark blue wax is made from shellac, mastic, calcined mica, Spanish chalk, and cobalt blue. Prussian blue is also used in sealing waxes.

Gold sealing wax is made with shellac, turpentine, rosin, mastic, and Dutch gold cut up fine. The color can also be obtained by using 1 part of silver leaf with six parts or shellac and one of white rosin. The brown color of the mixed resins imparts a golden tint to the silver. Gold leaf can also be used with chrome green in a wax made of shellac, rosin, and turpentine. Metallic lusters to sealing waxes are obtained through the use of powdered mica in the cheaper grades, and shades of bronze powder for the higher grades. Sometimes sticks are simply ornamented by brushing them with spirits of turpentine and then applying a dust of silver or bronze.

Green sealing wax is made with shellac, rosin, and turpentine, using gypsum, mineral blue, and massicot as the pigments. Chrome green and chalk are used in some green sealing waxes. The green may be a combination of blue and yellow pigments. Flake white is used in white, rose, or violet sealing waxes. A rose lake is used to obtain the rose color, and when blended with mineral blue produces a violet color. A vermilion color is obtained with cinnabar. Coal tar reds are ordinarily used in red sealing waxes. Yellow sealing wax is pigmented with massicot, or with chrome yellow, which colors can be let down with magnesia rubbed down in turpentine, and incorporated in Venice turpentine, shellac, and rosin.

A recipe by De Keghal[46] for a high-grade red sealing wax is as follows: Melt 7 kg of gum lac at a low heat with constant stirring, and then add successively 5 kg of Venice turpentine, 1 to 2 kg of vermilion, and 70 grams of magnesium carbonate. The mass is stirred vigorously and constantly to prevent the pigment from settling. A small globule is dropped on a glass plate and if color, hardness, and texture prove satisfactory, the flame is lowered to keep the mass just fluid, and 130 grams of Peruvian balsam are carefully stirred in. The mass is poured into "forms" of the desired shape and permitted to cool slowly. The wax is then polished and stamped with a warm stamp.

Brown sealing waxes require for their preparation mixed pigments such as lampblack and cinnabar, red bole and minium, or brown rotten stone

with or without cinnabar. Gypsum and magnesia are used as mineral fillers. Burnt sienna gives a reddish-brown shade.

A crimson sealing wax can be made from 2 parts of Venice turpentine, 4 of shellac, 1 of rosin, 1½ of carmine, and ⅒ part of magnesia mixed with oil of turpentine.

Transparent Sealing Waxes. A transparent (i.e. translucent) sealing wax is made from bleached shellac, mastic, and very fine, viscid light-colored turpentine. Carefully selected colors may be added if desired. For example, a plain transparent sealing wax can be made from 3 parts of bleached shellac, 6 of mastic, 3 of turpentine, and 2 of chalk. Zinc white may replace part of the mastic and the chalk to obtain a transparent white variety. Finely pulverized leaf metal, gold or silver, can be used for gold or silver transparent sealing waxes. Finely powdered yellow or bronze colored mica produces what is known as "adventurine" sealing wax.

Gums used for sealing waxes are selected carefully as to color, and often the original gum is decolorized by melting over a steam bath. If heated over a flame the gum loses some of its plasticity, although this loss can be offset by the Venice turpentine. A good grade of sealing wax should be clear, smooth, and brilliant in luster, and should melt without giving off fumes or disagreeable odors. It sould not soften so as to fall in drops, and after the impression is made, it should resemble the original wax in appearance. The seal should break easily and without crumbling.

Wax Bottle Seals. A bottle wax is used to bind a stopper to a bottle. In addition it sometimes functions as a tamperproof seal. Since this type of binder is used on spiritous liquors, it is desirable that it be very resistant to alcoholic liquids. For spiritous liquors a bottle wax may be made from *beeswax* 1, rosin 2, and pitch 2 parts. For the application of the wax, the neck of the bottle is dipped in the compound and turned horizontally. Red ochre, Berlin blue, and zinc chromate can be used as pigments to obtain red, blue, or yellow bottle waxes.

In the manufacture of bottle wax, it is customary to use a considerable amount of pigment, a resin, and a wax. Not all bottle waxes contain resin, and some contain pitch. In order to produce bottle wax at a low cost it is advantageous to use rosin, or to use waste resins as those obtained from the evaporation of the solvent washings of caoutchouc or crude gutta percha, as proposed by Jasinski[93]. A black bottle wax can be made by melting together rosin 6½, *beeswax* ½, and ivory black 1½ parts. A softer wax can be made by simply melting *ceresin wax*, and incorporating a considerable amount of lampblack.

A bottle wax, according to Braude[13], may be prepared from *carnauba wax* 30, *beeswax* 20, *paraffin wax* (m. 50–52°C) 20, whiting 1, baryta 10, and chrome orange 16 parts. The waxes are simply melted together and the

pigments stirred in. An asphalt sealing wax of Hughes[88] is made from asphalt 60, blown asphaltic base oil residuum 10, resin 14, *white wax* 5, and manganese dioxide 5 parts.

Tree Waxes. Cordray[35] devised a tree wax for protecting and healing abrasions of trees, which may be prepared from pine resin, *beeswax*, tallow, lime, and cottonseed oil.

Dutton[50] describes a wax emulsion which will protect living trees from sunscald, borer, and fungus injury, by treating the trunk and branches. The emulsion is aqueous and comprises *paraffin wax*, an ammonium salt of a drying oil acid, a colloidal earth, and finely divided aluminum. Waxes other than paraffin, such as *beeswax* or *carnauba*, can be employed. An example of the emulsion is as follows: ammonium linoleate (dissolved in 50 parts of hot water) 3, bentonite (smoothly dispersed in 50 parts of water) 3, and paraffin wax 10 parts. The ammonium linoleate solution and the bentonite dispersion are mixed at 70–90°C, and the molten paraffin wax slowly poured into the hot mixture; the resulting slurry is vigorously stirred until a good emulsion is obtained. When cooled the product is a creamy stock emulsion. A recipe for spraying is given as: stock emulsion 36, water 36, aluminum powder 7, water to complete 44, parts.

Grafting wax is a wax used for grafting a limb of one kind of a tree to that of another. It must be tough, and resistant to insect attack and weather. The wax is not unlike that of a black bottle wax. A recipe calls for *beeswax* 2, linseed oil 1, rosin 10, and powdered charcoal 1 part. The latter can be replaced in whole or in part by fuller's earth. A grafting wax for small plants can be made by melting together rosin with an equivalent amount of waxes comprising *woolwax*, *beeswax*, and *paraffin wax*, and a sufficient amount of kidney rosin oil is added to the melt to thin the composition when it is poured into cans.

Tree-Bands for Insect Control. Rolls of corrugated paper are saturated with a composition of an insecticide, a plasticizing oil, and wax. Tree banding material for insect control is also applied directly to the bark of the tree, that is, without the use of the corrugated band. The material for insect control should have good plasticity at low temperatures, should not run off at a temperature up to 45°C, should not stiffen at temperatures down to 5°C, should not be affected by wind, rain, or snow, and should retain a consistency sufficient to capture and hold the insect through the winter months.

German raw products of use in banding material include "Oxykresylcamphan" (oxycresylcamphan); "Kogasin" (a hydrocarbon mixture from water gas by Fischer-Tropsch synthesis); "Chlorokogasin" (same chlorinated to 52% Cl); "Oppanol" (isobutylene, $(CH_3)_2\,C = CH_2$ polymer, m. wt. 40,000); "Igevinen" (a polyvinyl ether); and "Uresinen" (a urethan formaldehyde polymer). The latter two can be used without castor oil

plasticizer, and the addition of oxycresylcamphan increases their stability. Banding material of any desired flow point can be obtained by use of the appropriate wax. Several formulas using the materials described are given by Pfaff.[133]

Waxes as Embedding Media for Tissues. Where a specimen is to be examined for its cell structure it was customary in the past to embed the specimen in *paraffin* wax, and then slice the whole into the tissue thickness desired by means of a microtome knife. Paraffine alone does not make a satisfactory embedding medium for animal or vegetable tissues, since the ribbon which is cut with a microtome from the block which holds the tissue will curl or roll in the cutting, making it impossible to handle the specimen properly for microscopic examination. It is for this reason that a paraffine-*bayberry wax*-rubber mixture has been used for both infiltration and embedding of the tissues.

Groat[75] found that a more satisfactory medium can be prepared by blending a synthetic resin of low viscosity with the *paraffine* or *ceresin* used. For example he cites a particular blend of paraffine (m. 56–58°C) with a water-white hydrocarbon resin (LX-291), produced by the Neville Company, Pittsburgh, Pa., as very satisfactory for the purpose. Excellent sections, which ribbon well, of any desired thickness below about 20 μ can be cut at room temperature.

The compositions of the paraffine-resin media are indicated by the percentage by weight of resin in the mixtures. Hardness of the media increases as the content of the resin increases. The mixtures are most readily prepared by blending the weighed portions of paraffine and resin at a temperature of about 170°C, and filtering. A paraffine oven set at 59°C is satisfactory for holding any of the melts.

Embedding of biological material for thin sectioning may be prepared by mixing pure *white beeswax* 1 part, with synthetic resin 2 parts. A synthetic resin of the type used for microscopic mounts should be selected.

Embedding material for micro-technique may be prepared from *paraffine* 200, rubber 2, and 0.5 parts beeswax. The rubber used can be prepared by air drying concentrated latex such as "Heavatex" in thin layers, and then cutting it into small pieces. The wax ingredients are melted together but the added rubber takes a number of hours to dissolve and is stirred occasionally. *Sealz wax* is simpler to use, as it has the rubber in combination with wax; about 10 parts of Sealz wax will replace 2 parts of rubber in the recipe.

Microcrystalline waxes are used for imbedding media but not for delicate tissues since they have too high a melting point and tend to dehydrate the tissue. Paraffin wax of 128/130°F melting point with 1 to 2 per cent of *'A-C Polyethylene #6"* added makes an excellent embedding medium since it yields a flat ribbon of good tensile strength when sliced with a

microtome knife. Best results are obtained by infiltrating tissues in pure paraffin, and imbedding in the harder medium such as a 5 or 10 per cent paraffin-resin medium, or in paraffin-"F-T Wax" medium. Invariably, as the medium becomes harder the range of thickness of sections which can be cut well becomes narrower and shifts downwards.

It is desirable to use a wetting agent in the fluid used to float the sections on the slide, especially for the thinner ones where incorrect infiltrating and imbedding media may result in production of fine creases in the tissue of the section.

Wax for Desiccators. A mixture of 3 parts of beeswax and 2 parts of petroleum jelly is recommended for making a perfect seal between the body and top of a glass desiccator.

Ornament Coating Wax. Figurines carved from wood and clothed with garments made of paper or fabric material are coated with wax, which preserves the painted structure. The wax composition in favor for dipping the figurines is one of *paraffine*, *ozokerite*, and a small amount of *candelilla wax*.

Ornaments, doll parts, unglazed china, earthenware, plaster, and like articles may be efficiently coated by dipping them in a liquid wax consisting of *paraffine* and *ammonium stearate*. The liquid wax heated to 120°C (248°F) is allowed to drain and cool from the object coated, then dipped again, and finally dipped in cold water to give a varnished or glossy appearance.

Wax Coating Meerschaum Pipes. Meerschaum, a hydrous magenesium silicate, entering commerce from Asia Minor and to a lesser extent elsewhere, is used for bowls of tobacco pipes and for cigarette holders. The natural nodules are first scraped to remove the red earthy matrix, then dried, again scraped, and polished with wax. The rudely shaped masses thus prepared are sent from the East to European manufacturing centers, where they are turned and carved, smoothed, and finally polished with a *white beeswax*. As the pipe is used by the smoker the color progressively changes to a brownish amber due to the beeswax with which the surface of the bowl had been impregnated in the polishing operation.

Waxing Thread. A waxing composition for use on threads and yarns, according to Houston[84], can be made from *paraffine* 16, *cacao butter* ½–1, and *sperm oil* ¼–½ parts.

WAX IN SHOE-POLISH PASTES

Shoe polishes have been packaged in a variety of containers—can, glass and even collapsible tube, but paste types in "tins" (small two-piece circular metal boxes) are the largest sellers.

Paste-type polishes containing *carnauba wax* were marketed as early as 1885. They were introduced by Whittemore Brothers Corporation, Cambridge, Massachusetts, a more than a century old shoe polish maker. Shoe

creams are paste-type polishes that may be applied to shoes or leather goods and rubbed to a high finish with a soft brush or polishing cloth. Combinations of different waxes are used in shoe polish formulations. The waxes are referred to as "hard" and "soft." This classification today seems to be based more upon their characteristics as to absorptive capacity of solvent, solvent retention, setting up value, body, consistency, film thickness, luster, rapidity of drying and shining, and keeping quality in the tins, than upon the actual hardness of the wax.

In the "hard" class, regularly used are *carnauba wax*, *ouricury wax*, *hard paraffine* (e.g. Fisher-Tropsch waxes), and *candelilla wax*; also waxes which have been exploited to a limited extent, such as *sugarcane wax*, *ricebran wax*, *sisal wax*, *douglasfir bark wax*, and a few synthetic waxes. The "soft" waxes comprise *crude montan wax*, *beeswax*, *ozocerite*, ordinary *paraffine*, *anhydrous lanolin*, and *japanwax*. In the making up of a shoe polish it is necessary to build up a wax formulation in which the hard and soft waxes are properly proportioned.

In the formulation of a shoe polish paste, attention is particularly given to the individual characteristics of a component wax. For example, montan wax has a good binding power for solvent, carnauba wax has one of the worst; ozocerite, "Aristowax," and paraffin have excellent solvent retention power; carnauba gives the highest polishing, that is, higher than shellac, candelilla, and synthetic waxes. Waxes from the family of grasses, such as *esparto*, *henequen*, and *broomcorn*, might do quite as well as carnauba in the shoe-paste polish formulations, were they commercially available. *Douglasfir wax* has the greatest solvent retention power of any wax and produces the smoothest rubbing qualities, although it lacks the hardness and luster of *carnauba wax*

Turpentine is the best solvent for the mixed waxes, but turpentine substitutes within the boiling range of 130–190°C are generally used to thin out the 1:1 mixture of wax and turpentine to the consistency desired. The behavior of some waxes in turpentine is somewhat superior to that in mixed solvent such as 1:1 mixture of turpentine and "Varnolene," whereas other waxes work out about as well in mixed solvent as they do in turpentine alone. In formulations turpentine substitutes are referred to as white spirits, Stoddard solvent, benzin, "Varsol," etc.

The general procedure in making a shoe polish is to melt the hard wax in a double-jacketed steam kettle; add a solubilized color (e.g., nigrosine base processed with raw montan wax and olein), mix and stir in the soft waxes which have been melted separately. The turpentine is added at a temperature of 80°C, completing the thinning with Stoddard solvent, benzin, tetrolin, or the like. The temperature is permitted to drop to 48–52°C for filling in the cans of "tins."

Some shoe creams on the market have shown serious faults, such as in-

crustations developing on the surface, sweating of the cream sufficient to corrode the tin, granulations throughout, and shrinkage sufficient to make the shoe-paste polish rattle in the tin. These defects result either from lack of experience or carelessness in their manufacture—or from a deliberate cheapening by the use of inferior ingredients, or an attempt to shorten the length of time required to produce a good product. When a tin is opened, the surface should have a "mirror finish," and not a "veiled bloom;" and the cream should retain its consistency over a prolonged period of use. The proper selection of waxes, the proportion of soft to hard waxes, the kind and proportions of solvent, the filling temperature, the degree of chilling, and the temperature of storage of the tinned polish, are important factors that must be carefully considered in marketing shoe creams.

The following are formulations that have been suggested for American shoe polish pastes.

(E) Crude montan wax 32, carnauba wax 25, ebony Utahwax 3, paraffine flakes 55, processed nigrosine 11, and turpentine substitute 300 parts.

(F) Crude montan wax 22, carnauba wax 22, stearic acid 8, nigrosine black 4, ceresin 60, and turpentine substitute 300 parts. The waxes are melted together, and the stearic acid and nigrosine stirred in. The mixture is cooled to about 40°F before pouring into the tins.

(G) Double refined montan wax 50, crude scale wax (m. 53–54°C) 20, candelilla wax 10, carnauba wax (#3 NC) 10, processed nigrosine 10, and turpentine 260 parts.

Double refined montan wax is said to provide good solvent retention, good binding power, and better gloss; it promotes a glossy surface and despite its softness gives no tack and will not attract dust. Beeswax promotes cohesion of waxes without tack. The vehicle most prized for use in shoe polish pastes is turpentine of 310–319°F boiling point. Stoddard solvent (a dry cleaner's naphtha), "Varsol," and "Varnoline" are extensively used. Stoddard solvent has a boiling range of 300–410°F. Tetrolin is used mostly in Europe where turpentine is not readily available. Kerosene (b. pt. 350–416°F) is also sometimes used in conjunction with turpentine. The use of solvents containing 15 to 30 per cent of gum spirits of turpentine is quite common.

Goldreich[71] specifies a polish for boots, leather articles, etc., which has both waterproofing and preserving action, as preparable from gilsonite, *esparto wax* or *candelilla wax*, turpentine, and oil of mirbane as an odorant. Odorants for shoe polish are nitrobenzene, trichlorobenzene, and orthodichlorobenzene. The latter two are added in quantities of ½ of one per cent. The dyes added range from 1 to 3 per cent.

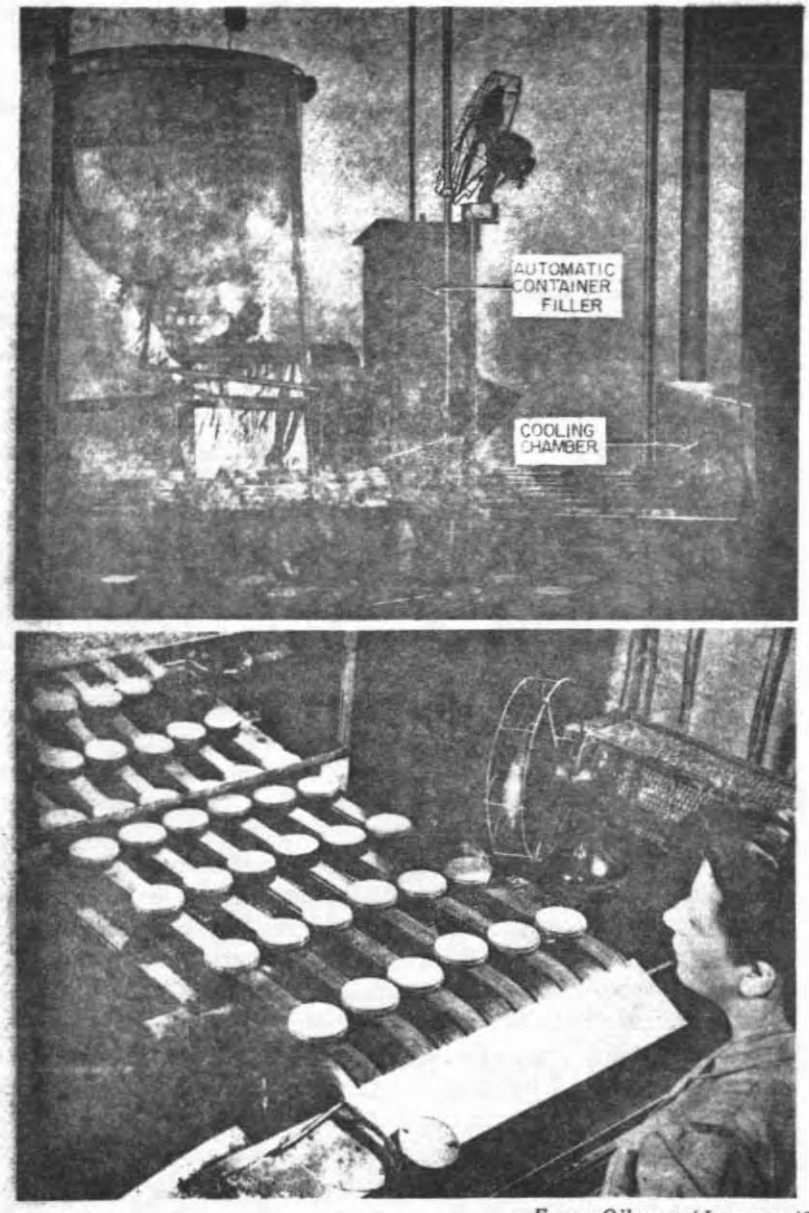
Water Cream Polishes. In the water cream polishes, water is used in conjunction with turpentine and an emulsifying agent, commonly a sodium or potassium soap. The waxes are melted and the organic solvent added

while stirring. Water is brought to a boil in a separate kettle, the soap dissolved in it, and the wax-solvent mixture poured into the boiling water, with vigorous stirring. An example is given in a recipe by Davidsohn[40]; *carnauba wax* 10, *beeswax* 3, *paraffin wax* 10, potassium soap 3, turpentine 15, Stoddard solvent 12, and water 47 parts.

A light neutral water-containing cream polish can be prepared by heating together triethanolamine stearate 25, *beeswax* 10, *candelilla wax* 30, *carnauba wax* 40, turpentine 20, and water 50 parts. The melt is made at 200°F and poured slowly into the hot water at the same temperature, stirring vigorously. If a colored shoe cream is desired, some oil-soluble dye is stirred in the wax mixture while the latter is melting. Shoe creams for white leather contain about 8 per cent of zinc oxide. Titanium oxide is also being used as a whitening agent in such polishes.

White Shoe Cleaning Paste. This type of paste may be prepared from titanium oxide 5, lithopone 40, dextrin 6, borax 1, water 48, *candelilla wax* 2 parts, and a little bluing. The wax must be melted in the hot borax solution, the dextrin added, and the pigments added last. This paste can be pressed into tubes. Many of the water cream polishes employ potassium carbonate and rosin as the emulsifying agent to disperse the waxes in water. A shoe cream of the water-base type can be prepared in which an oleaginous-resin complex is employed as a permanent emulsifying agent. A typical formula would be of the following order: O-R complex 4, *carnauba wax* 1½, *candelilla wax* ¾, *ceresin* wax ¾, turpentine 4, lemongrass oil 0.4, light mineral oil 0.6, and water 88 parts.

Production and Packaging Paste Type Polishes. The waxes such as carnauba, beeswax, and high melting paraffin are melted together in a 100-gallon steam-jacketed mixing kettle. The high-boiling naphtha solvent, or turpentine substitute, is pumped to the kettle only after the coloring material has been incorporated in the melted waxes. After mixing the polish in its liquid state, it is allowed to flow from the bottom of the kettle through a gate valve down into the hopper of an automatic filling machine, which may be located on the floor below. When the hopper is filled with the warm (125°F) liquid polish it passes down into the filling head cylinders of the machine. The tube of the filling head is automatically inserted close to the bottom of the container, or tin, and then carefully withdrawn to avoid bubbles and cause irregularities in the surface. Whole rows of flat round tins of 1½ to 2 ounces capacity, are filled on a conveyor belt which runs through a cooling tunnel employing an air current to aid in the setting. At the end of the filling line, the tins are inspected for overflow and underfilling by a worker observing them through a mirror. The tins then slide onto a long single belt conveyor. Electric fans along the conveyor route help to hasten solidification; artificially chilled air aids in the cooling, although any extreme chilling must be avoided. Tin lids are applied by a



From: Oilways (January 1947)

FIGURE 39. In the preparation of shoe-paste polishes, the waxes are melted in a double-jacketed kettle and the processed color added. *above:* The shoe-paste polish, fluid at 125 F, flows from the kettle to the automatic container filler, and the filled tins are conveyed through the cooling chamber. Squat glass jars are sometimes used instead of tins. *below:* The appearance of the shoe-paste polish is judged by the surface ring formation and gloss. The uncapped tins are inspected through a mirror in this instance.

capping machine. It is customary to pack 12 tins to a carton and 12 cartons to a shipping case.

The appearance of the shoe cream on opening is often judged by a characteristic of surface ring formation and gloss which comes about through the use of a good quality of carnauba wax with an appropriate solvent, accompanied by proper precautions relative to the rate of solidification before the tin is capped. The filling operation is best carried out in an air conditioned room, but in the absence of air conditioning equipment it is important to exhaust the fumes by suitable exhaust fans. If the cream is packaged in tubes a softer cream is prepared for the tube filling machine.

The gross sales of American shoe polish pastes and dressings have been estimated as exceeding $25,000,000 per annum.

Black Shoe Pastes. The formulations of shoe paste given below are those of German manufacture:

(A) "Gersthofen Wax OP" 8, carnauba wax 25, raw montan wax (Riebeck) 6, candelilla wax 8, nigrosine base 6 prepared with raw montan wax (and olein) 18, and paraffine (m. 50–52°C) 29 parts. Total 100 parts. The proportion of wax foundation to solvent (tetrolin) in the cream is 1:2.5 to 3.5.

(B) Carnauba wax 11, raw montan wax 20, shellac wax 16, double refined montan wax 4, nigrosine base 5 with stearine 10, ozocerite 2, and paraffine (m. 50–52°C) 32 parts. The proportion of wax to solvent is 1:3 to 4.

(C) Carnauba wax 20, shellac wax 22, nigrosine base 3 with raw montan wax (and olein) 9, ozocerite 3, and paraffine (m. 50–52°C) 43 parts. The proportion of wax to solvent is 1:2.5.

(D) Carnauba wax 6, raw montan wax 33, shellac wax 4, yellow beeswax 3, nigrosine base 3.3 with stearine 6.7, paraffine (m. 50–52°C) 44 parts. The proportion of wax to solvent is 1:2.5 to 3.

Colored Shoe Creams. Typical formulations of colored hard shoe creams of German origin are as follows:

Wax	Shoe Cream A	B	C	D
		per cent		
Gersthofen Wax OP"	6.5	22.0	—	—
Gersthofen Wax CR"	12.8	—	16.5	14.0
Montan wax	25.6	26.0	24.5	22.0
Shellac wax	1.6	—	2.0	5.0
Gersthofen Wax BJ"	—	—	3.5	6.0
Oil-soluble color	9.5	13.0	11.5	11.0
White ozocerite	6.0	4.0	5.0	7.5
Paraffine (50/52°C)	38.0	35.0	37.0	34.5
Total	100.0	100.0	100.0	100.0
Wax to solvent ratio	1:3	3:4	2:3	2:1

German water cream polishes have been prepared from semirefined montan wax 13.7, beeswax 1.0, japanwax 1.0, colophony 3, paraffine (50/52°C) 2.0, and oil-soluble color 1.0; plus a solution of potassium carbonate 2.2 and water 34.0; plus a solution of nigrosine (water-soluble) 3.2 and water 38.5 parts. Perfume may consist of 0.5 part of oil of mirbane.

WAX IN SOUND RECORDS

The Early Use of Wax in Sound Records. Under the term "sound records" we include both recorders and reproducers of the phonograph and gramophone type. A gramophone is an instrument for reproducing sound by transmitting to the air the mechanical vibrations of a stylus in contact with a sinuous groove in a moving record. Wax is used in the wax-cylinder phonograph of Edison, and in the making of the recorders of the improved flat record type of Berliner. Originally a glass disc was covered with a semi-fluid coating of ink or paint, in which the stylus cut a sinuous spiral running from the outer edge of the record to the center, or vice versa. A turntable carried the record disc, and was rotated by suitable means. Berliner's next step was to make a record in a solid material by direct etching. A disc or cylinder of zinc or glass was coated with *beeswax* dissolved in benzin. Beeswax was selected because it offered little resistance to the moving stylus and withstood the chemical action of the etching acids. When the recording stylus had traced out its line on the record, and exposed the solid disc below, the latter was etched and a permanent record produced. Copies could be made by the galvano-plastic process, by making a matrix, and impressing the discs of hard rubber or the like.

Sound Record Compositions. Improvements are continually being made in the working out of details in the art of sound recording and reproducing. Instead of plain beeswax, compounds of various waxes are used in producing the recording wax, for example, *ceresin*, *cornauba*, *candelilla*, "F-T Wax," paraffin and *microcrystalline waxes*, as well as beeswax. Wax of some kind is also included in polystyrene formulations of the compounds used in producing the talking machine or reproduction records. A composition suitable for use in making sound records is given as paraffin wax mixed with hydrogenated castor oil, and a suitable filler, such as barium sulfate or clay. Ellis[68, 55] refers to the use of *stearic acid*, asphalt, pitch, talc, etc., as sound record composition ingredients.

Phonograph records have been made from a composition of powdered slate, thermosetting resin, gas black, and pitch, with two per cent each of *calcium stearate* and *montan wax*. Gramophone records may be made from a laminated paper material impregnated and surfaced with a composition of shellac, resin, a hard wax, and acetylene black. The discs when molded have considerable strength and flexibility.

A composition for sound recording is given by Schuh[146] in which *stearic* acid 60, *montan wax* 13, sodium carbonate 5, basic lead carbonate 8, and a plasticizer such as methyl abietate 14 parts, are compounded together.

According to Clare[30] an improved phonograph record having a grooved reproducing surface can be made of a homogeneous thermoplastic binder composition consisting of cellulose acetate, plasticizer, resinous pine wood extract, a phenolic aldehyde fluxing resin (drop point 65–95°C), wax, and filler. The composition is preferably produced by melting the cellulose acetate and plasticizer, adding the other ingredients, molding the product in the form of biscuits, and impressing the sound track thereon with a conventional record press. Clare claims these records have improved resistance to wear, freedom from needle noise, and high fidelity of reproduction.

The plasticizer may be dimethyl phthalate, triphenyl phosphate, or other suitable chemical. The wax may be *carnauba*, *candelilla*, *montan*, or *microcrystalline hydrocarbon*. The filler may be china clay, silica powder, carbon black, or other suitable substance.

Treatment of Sound Record Surfaces. Wax surfaces for preparing gramophone matrices may be silvered chemically or sputtered with gold or silver before electrolytical deposition of the copper to form the master shells, according to a process outlined by Majumdar[112].

Resurfacing of phonograph records is effected by wiping the phonograph cylinders with a solvent such as kerosene, and then wiping the record with a mixture of alcohol, ether, and vinegar, so that the record tracing is entirely obliterated.

Method of Producing Flat Records. A sound record is originally made in wax, e.g., a compound of *ceresin*, *beeswax*, and *carnauba wax*; a reverse is molded from it in clay or plaster; a copy of the original is molded from the clay or plaster in more durable material such as type metal; a steel negative is pantographed from the latter and a thin sheet of metal is pressed into the steel copy. If desired, the clay reverse may be hardened by firing, and used as a working basis for forming records, as suggested by Head[83].

In the production of phonograph records the original recording is made in a wax blank, is then coated with a metallizing powder, and subsequently electroplated with a suitable metallic deposit, which, after being removed from the wax and backed up by copper, serves as a master matrix. The metallizing powder is necessary to make the surface of the wax electroconductive. These powders are made of an alloy of 90 per cent copper and 10 per cent zinc, the tackiness of the alloy powder being aided by the addition of about 0.1 per cent of *stearic acid* as suggested by Hunter[89].

Molded sound records for reproduction, as on talking machines, are formed with a hard surface material capable of softening slightly when heated; e.g., a phenolic condensation product, a backing material more

plastic when heated then the surface material, and a sheet of fabric between the surface and backing materials. The backing may be formed of wood flour and an equivalent amount of fusible phenolic condensation product or shellac or rosin, as described by Aylsworth[10]. Gramophone disc records are formed of finely ground wood, with or without the addition of flock or shoddy, and binding material such as shellac. The dry material is jigged to produce a level surface, is dampened by steam, and slightly compressed to form a disc, which is dried and subjected to a higher pressure in a hydraulic press, as described by Millar[17]. Coloring matter may be added to the composition, such as azine, induline, or nigrosine. A binder of shellac-like composition can be prepared by combining copal resins with polyhydroxy fatty acids, e.g., trihydroxystearic acid, dihydroxystearic acid, etc.

WAXES IN THE TEXTILE INDUSTRY

Textile Processing. The natural fibers, such as wool, cotton, and silk, contain a certain amount of natural wax or wax like material which acts as a protective agent from atmospheric influences and also forms a natural lubricant. Such waxy material is removed by subsequent scouring of the fibers to assure uniform dyeing or bleaching. In the scouring or boiling operation there results a loss of softness, pliability, and elasticity of the fibers, which makes it necessary for the textile processing industry to treat the fibers or finished yarns with waxes or wax-like materials.

Yarns are sized with a starch, gum, or other suitable material to increase the tensile strength. The sizing, however, diminishes the elasticity and softness, making it necessary to introduce a wax in the sizing. The nature of the wax used will depend somewhat upon whether it is to produce a nonpermanent effect, that is, one which will be removed from the yarn or fabric in a subsequent operation; or a permanent effect which may be desired to give the finished goods or yarn a high luster, softness, and water repellency. Waxes frequently used as adjuncts to sizing are *japanwax*, *beeswax*, *spermaceti*, *paraffin wax*, *petroleum ceresin*, and *tallow*.

The utilization of synthetic fibers in the textile industry during recent years has introduced many problems concerning the elimination of friction between fibers and machine parts, or between the fibers themselves. Friction breaks threads or fibers in the process, resulting in costly stoppages; it also causes uneven feeding or winding of threads, resulting in inferior finished fabrics. Elimination of friction, in practically every phase of handling textile fibers, is considered one of the major problems in practical mill procedures, covering viscose, cellulose acetate rayon, nylon, and blends of synthetics with natural fibers such as wool, cotton, and silk.

The textile manufacturer frequently finds it necessary to combine a softening action with lubrication, in order to obtain a more uniform weave or

stitch and produce a fabric of desirable texture and feel, that is, the "hand." The nature of the lubricant must be such that it will not only lubricate and soften the fibers, but also eliminate the friction previously referred to; it must control the static as well. In modern practice self-emulsifying waxy solids are effectively used. A suitable waxy solid for this purpose is one which will produce an emulsion with high-solids content of sufficiently low viscosity to insure ease of handling and to keep the moisture added to the fiber at a minimum.

Certain synthetic waxes which are self-emulsifiable because of their low interfacial tension characteristics, such as complex esters and ester-ethers stemming from hexahydric alcohols, alkylene oxide, and common fatty acids, belonging to the class of nonionic surface-active agents, meet the requirements of the textile manufacturers as to the requirements outlined above. A waxy solid of this nature is known under the trade name of "Avcolube."

"Avcolube 100" (Atlas Powder Company) is a light tan colored waxy solid, with a titer value of 35–40°C, specific gravity 1.04–1.09, flash point 425°F, and fire point 519°F, and which is dispersible in water, insoluble in acids, saponifies slowly in a weak sodium hydroxide solution, is soluble in warm vegetable oils and mineral oil, insoluble in mineral spirits, insoluble in methanol, but slightly soluble or dispersible in many organic solvents.

When fibers are dyed before carding and spinning, "Avcolube" can be effectively used as a lubricant and antistatic agent. The wax is conveniently applied to the dyed raw stock at the end of the dyeing cycle in the last rinse, thus eliminating need for additional processing or handling. The required amount of wax is first emulsified by stirring it into warm water (60°C), and then this emulsion is added to the rinse bath.

Treatments for Rayon Yarn and Fabrics. Water-repellent finishes are applied to textiles for the purpose of maintaining water repellency after several launderings or dry cleanings. For example, a rayon fabric is bathed in a water solution containing 5 to 20 per cent of a composition prepared from *ceresin wax* 20, *stearic acid* 10, triethanolamine 5, and water 65 parts. After drying, the fabric is bathed in water containing water-soluble melamine-formaldehyde precondensate, aluminum acetate, and acetic acid. The fabric is dried at 120–150°C. Cook and associates[34n] have also given other two-bath processes for rayon and wool, in which *paraffin wax*, *octadecamide* (stearamide), and various chemicals are used. The application of 0.5–2.0 per cent of wax or the weight of the dyed goods will satisfy most requirements.

Newer types of synthetic waxes are applied from a solvent solution instead of the customary water emulsion in lubricating rayon yarns. The solvent permits the wax to penetrate faster and more thoroughly into the

yarn. It also eliminates the necessity of drying treated yarns, since the solvent evaporates readily. In the process of treatment the rayon yarn is soaked in the solvent solution of the wax; the wax pick-up is regulated according to mill experience, a greater amount being used in full-fashioned knitting than where there is a minimum of twist setting and protection necessary. A synthetic wax that is extensively used for the purpose is "Avconit 3" (Atlas Powder Company) which is generally applied from 25 to 50 per cent solutions in Stoddard solvent at about 65°C (150°F) to obtain 3 to 10 per cent wax deposit in the yarn. Low molecular weight polyethylene polymers of the wax type have also been used for the purpose.

The estimated consumption of petroleum waxes for textiles in 1953 was in excess of 20,000,000 pounds. The annual consumption of special synthetic waxes in the textile industry is estimated to exceed 200,000 pounds.

Tent Cloths and Tarpaulins. Tent cloths and tarpaulins are generally rendered fireproof, waterproof, and mildewproof by treating the fabric with an impregnating coat of pigment, resin pitch, and chlorinated wax. For example, the coating may be a mixture of phenolic resin, tin oxide, pitch, and *chlorinated paraffine*. The color, a tone of green, is ground in the mixture. The composition after its application should show no more than a faint color impression when white paper tissue is pressed on the surface of the cloth. It has been roughly estimated that 15,000,000 pounds of wax per annum is used for tent cloths and tarpaulins. (For use of scale wax in the fabrication of cotton duck and canvas, see Scale Wax, p. 398.)

WAX IN THE TOBBACCO INDUSTRY

Waxing of Tobacco. Many tobacco blends are lightly sprayed during manufacture with mixtures called "casing solutions" (glycerin, licorice, etc.), that control their moisture content and affect the rate of burning or may impart a certain aroma or taste. Ordinarily casing emulsions contain low-viscosity white oils, but no wax. Harsh tobacco may be rendered mild by treating it with a wax emulsion to preserve the moisture, relieve irritant products, and cause the tobacco to become mild.

The matured leaves of the green tobacco plant are normally prepared for consumption by curing, that is, by exposing the leaves to air, sun, or fire. The cured leaves are allowed to absorb moisture until they become pliant. The tobacco leaves are then assorted and packed in boxes, hogsheads, or bulk, where the tobacco undergoes a slow fermentation that develops the aroma and flavor. Afterwards the tobacco is worked up in the various forms suitable for the market. When overdry tobacco is ignited, products irritant to the smoker's throat and nose are formed, which may be offset by providing an adequate moisture content by spraying it with a wax emulsion. According to Andrews[9] the loss of moisture can be checked, and a harsh

tobacco made to lose its irritating properties by treatment with wax, and as a resultant effect the tobacco becomes mild when smoked in any form.

The emulsification of the *paraffin* or other wax in water, for the tobacco treatment, is brought about with the aid of an emulsifying agent, e.g., stearic acid with triethanolamine, or simply *diglycolstearate*. Andrews[9] states that it may be desirable to oxidize the impurities out of the emulsion, if any, by means of potassium permanganate, before applying the emulsion.

Tobacco called "Black Fats" makes use of USP petrolatum. "Black Fats" is used for both smoking and chewing by the Negroes of southern Africa and the West Indies, and, to a limited extent, in the southern part of the United States. It is made of large-leaf dark tobacco treated with a petrolatum of extra light amber color, having a melting point of 113/123°F (Saybolt). After treatment each set of leaves is folded lengthwise and packed in small casks using a hydraulic press. The casks are stored in a heated chamber for a few days to permit complete permeation of the petrolatum mixture through all the tobacco. When removed from the cask, the leaves are quite black and pliable.

WAX IN VARNISHES AND PAINT MATERIAL

Wax in Varnishes. Waxes are used to some extent in both air-drying and heat-drying varnishes. In air-drying varnishes they can only be used in minute quantity as they interfere with the drying. Their more extensive use is in the baking varnishes, some of which are referred to as "slip varnishes."

Candelilla wax is incorporated to the extent of about ½ per cent in a varnish for finishing linoleum to a luster. Wax may be used in varnish that is applied to lithographed tin sheets that are oven dried and then fabricated into caps for glass containers, the wax furnishing the necessary lubrication to the dies of the stamping press so that the work is free from scratches and imperfections that would otherwise result. So-called "Drawline Varnish" has wax incorporated in it. The kind of wax used in a varnish varies with the kind of use to which the varnish is put. High melting point waxes such as *carnauba*, *montan*, ane *microcrystalline* wax have been used. Artificial ceresin has been used in metal decorating varnish. These waxes bloom to the surface as the varnish film dries. It is customary in the preparation of the varnish to cook the resin and oil together, and add the wax after dropping the temperature, and before adding the naphtha or other reducer to thin, or to add it while thinning.

Paraffin or *ozocerite* wax is sometimes incorporated in a varnish to increase the flexibility of the dried film. These waxes are used to the extent of one per cent or less of the nonvolatile content for coating papers, etc., without inducing the wax to bloom from the surface coated. An amount of

wax from 1 to 6 per cent is incorporated in the varnish when it is desirable to have the wax bloom out on heat drying a varnished surface.

Waterproof Label Varnish. In a varnish for application to absorbent paper labels with inked surfaces, *paraffin wax* can be advantageously employed. An example is: Batavia gum damar 63, tung oil 72, kerosene 33.7, cobalt drier (6%) 417, paraffin wax 1.6 parts. The resin is cooked with the oil to 450°F. The kerosene, drier, and wax are added in order, and the whole allowed to cool. The varnish is colorless and dries with a good gloss.

Wax in Paint Material. Wax is not extensively used in ordinary paint material. Artists' oil paints are occasionally emulsified with a wax which has at least been partially saponified. The wax, which must be of a saponifiable type, is dissolved in turpentine and then saponified by treating it with ammonia or an ammonium salt. The excess of the saponifying agent is then removed by heating. Wax does find use in the making of bronze powders; the waxy property of *stearic acid* is of particular value aside from its negative potential property.

Wax, customarily *slack wax*, is an ingredient of colored coatings made from casein and pigment, used in the coating of gloss papers produced for packaging chocolate candy bars. The paper is double coated with the pigmented coating and receives its gloss by being rubbed crosswise with a bar of flint by a mechanical reciprocating motion. These polished papers are produced in colors, inclusive of chocolate-brown, and find an extensive miscellaneous use.

Polishing Paints. For some purposes it is desirable to apply paint on which a design can be effected by polishing, and which can be washed or scrubbed without removing the design. Gargen and Ernst[66] have invented a paint containing wax for such a purpose. For example, one of their paints has the following composition: lithopone 61.5, aluminum silicate 8.8, *beeswax* 0.4, "flatting varnish" 20.1, and boiled linseed oil 9.2 parts. The amount of wax incorporated customarily not over 0.5 per cent is the optimum quantity that can be used without getting a waxy or greasy finish which would retard drying and make it difficult to repaint. The wax improves the washability of the painted surface, giving a surface which can be cleaned without marring the design. "Flatting varnish," referred to above, is a varnish composed of soybean oil 10, tung oil 10, East India gum 15, and mineral spirits 65 parts.

Mar resistance and water and salt spray resistance in air-dry paints and varnishes may be improved by incorporating ½ per cent of powdered "*Acrawax C*" in the grinding and mixing. In nitrocellulose sealers and topcoats the "Acrawax C" (beads) are dissolved in hot toluene which is added with rapid agitation to the nitrocellulose wetted with cold toluene.

Paint Removers. Paint removers are customarily made by mixing a

polar with a nonpolar solvent, such as acetone and benzene, to which mixture is incorporated a small amount of wax, commonly paraffin wax, to aid in solvent retention, and a chemical reagent either of an acid or alkaline character. Ellis[54] preferred ceresin to paraffin wax, and proposed the formula: tetrachlorethane 40, light camphor oil 25, denatured alcohol 35, and *ceresin wax* 2 parts. "Aristowax" makes an excellent solvent retainer. *Beeswax* has also been occasionally used in paint removers, but has little value as a solvent retainer.

Palm wax or *candelilla wax* is of value as a thickener in paint removers, and these waxes are used with or without the addition of paraffin. In the Harris[80] paint remover both paraffin and candelilla waxes are employed; e.g., phenol 10, *candelilla wax*, *paraffin wax* 1, and alcohol or acetone 87 parts. In the Wilson and Bacon[175] paint removers only the harder waxes are employed, and are kept in colloidal suspension by the use of phosphoric acid. A paint remover of this type can be prepared from benzene 46, methyl acetone 46, concentrated phosphoric acid 6, and *palm wax* or *candelilla wax* 2 parts; the wax is added last. The phosphoric acid increases the energetic action of the remover on linseed oil paints. Concentrated formic or glacial acetic acids have also proved to be effective wax-colloiding agents, and aid in removing films of linseed oil paint.

In an Ellis[54a] formula patented in 1916 the paint and varnish remover comprises denatured alcohol 55 gals., *ceresin wax* 20 lbs, aniline 10 lbs, and "light magnesia" 10 lbs.

OIL-SOLUBLE COLORS FOR WAXES

Ordinary dyestuffs and mineral colors are not soluble in waxes, nor are they soluble in oils. Therefore to color waxes it is necessary to use the so-called oil-soluble colors, for example Oil Yellow C Conc., Oil Brilliant Yellow, Oil Orange R Conc., and CCCC Oil Orange RG. One pound of the latter is sufficient to color 1000 pounds of a ceresin wax. In the blue range Oil-Soluble Blue S, an expensive brilliant blue of the alizarin series, and a cheap blue known as Oil-Soluble Dark Blue of the stearic acid type are available. Some of the recommended dyestuffs include Wax Yellow Extra, Wax Red G Conc., Wax Green G, and Wax Violet, all of which may be dissolved directly in the molten wax.

Although the yellow and orange oil-soluble colors prove satisfactory, Proell contends that pink, violet, and other pastel shades do not, and he has now provided a new series of dyes which are substantially soluble, sunproof, and heatproof to temperatures of 250°F or more. Proell[126] incorporated into the *paraffin wax* metal organic dyes, such as colored metal oximes, particularly metal alkyl gloximes. The alkyl radical dimethyl, diethyl, and the like, and a heavy metal, nickel or cobalt are employed.

An example is given by Proell: "A paraffin wax-stearic acid mixture containing 25 per cent of *stearic acid* was heated to 250°F and 0.005 per cent of nickel dimethylglyoxime and 0.01 per cent of dimethylglyoxime added. The latter dissolved rapidly to form a yellow solution. This solution was filtered and chilled to just below the melting point of the wax without any deposition of the dye. Cakes of wax cast from this solution remained colorless until they had cooled further, when a pink color developed. The shell pink wax so prepared has an intensity of color equivalent to that produced with 0.02 per cent of Rhodamine B dye, but of a more violet tint.

"The necessity for heating the wax to about 250° F in order to secure a homogeneous solution may be avoided by dissolving nickel stearate in the paraffin wax base and adding a solution of dimethylglyoxime in melted paraffin to the mixture. Cobalt used in place of nickel produced a tan colored candle."

Proell further states that he had found that metallic salts of 8-hydroxyquinoline, for example, the bismuth and ferric salts, dissolve readily in paraffin wax compositions and give intense colors, the bismuth salt producing a lemon yellow color and the ferric salt a deep brown. Other metal organic compounds, such as metal salts of alpha-nitroso beta-naphthol, are further examples of compounds suitable for use as dyes in paraffin wax compositions. The cobalt derivative of the latter compound gives a dull orange color and the iron alpha-nitroso beta-naphthol a tan color to the wax.

MISCELLANEOUS USES FOR WAX

Household Wax. A translucent *paraffin wax* of 130–132°F AMP, or thereabouts, is packaged in ¼-lb cartons by the Esso Standard Oil Company, Bayonne, New Jersey, under the designation "Esso Household Wax." For use, the label states that it be melted in a double boiler or over a pan of water, and not directly over a flame. Its recommended uses are for preserving, laundry, and miscellaneous. In the preserving of jelly and jam, the melted wax is poured over the contents in the jelly glass, or fruit jar, while still hot, and the capped glass container may also be dipped in the melted wax to obtain a superior seal.

In the laundry 1 to 2 teaspoonfuls of melted wax are stirred in each quart of starch, and then boiled for 5 minutes. This gives an improved finish on ironed articles. It is also used to keep the iron bright and smooth, in which instance a piece of the wax is wrapped in cloth for proper application. Miscellaneous uses include rubbing nails and screws with wax to make driving easier and smooth; coating the blade of a shovel with wax to keep snow from sticking to it; rubbing wax on the sides and guides of drawers to

help prevent sticking; and coating the interior of new flower boxes with melted wax to protect them against rotting.

Wax Method for Defeathering Fowl. Paraffin wax is used for defeathering chickens and other fowl. After appropriate bleeding, the bird is dipped in hot wax, and placed in a water tank to chill. The pins, feathers, fuzz, and wax are then removed by a small rubber-fingered picking machine. As the fowl is dipped, a coating of solid wax forms at once on the surface of the skin. The insulating value of this coating is high and thus the skin is protected against excessive heating and injury.

Wax Coating of Concrete Tanks. A suitable protective coating for the inside surface of concrete tanks in California wineries has proved to be *microcrystalline wax*. It remains flexible even at very low temperatures and does not crack or chip, owing to expansion and contraction of the surface. The slight tackiness of the wax causes it to adhere tightly, forming a strong bond with the concrete. It is highly impervious to water and dissolved gases (CO_2) to which it is exposed when the wine is fermenting. According to to Schreffler[145b] a patented gun is used to spray the melted wax, electrically heated almost to the flash point, surrounded by a stream of hot air also electrically heated to a higher temperature than the wax. New concrete can be coated immediately after it is cured and dry. Wax-lining of tanks costs 13 to 15 cents per square foot, inclusive of cost of wax (11 to 17½¢ per lb). In June 1947 a 16,000-gallon open concrete fermentation tank at the Roma Wine Company's Fresno Winery was coated with a microcrystalline wax of 170/175°F melting point. After three years of satisfactory use 40 more tanks of various kinds were spray coated with wax. One winery has lined concrete sherry cooking tanks with wax.

Waxed Coolers for Soft Drinks. Coolers for soft drinks can be waxed on the inside to make them waterproof. It is particularly important to wax the metal surfaces at the water level and the lid. Before the wax is applied the moisture around the cooler lid, topside, underside, and hinges is wiped dry, and then every two weeks the whole area is wiped over with a rag soaked in liquid wax. A liquid wax known as "Plasti-Coat" is used for the purpose.

Wax Type Pipe Coatings. Wax type coatings with a softening point from 125 to 170°F are applied to pipes, such as gas pipes. The coatings have a very low water absorption and high dielectric strength. They can be readily applied by machine, in a manner that the waxed surfaces are homogeneous and free from pits. Chemical rust inhibitors can be added to the paraffin wax and a wrapper or reinforcing material applied when needed.

Waterproofing Building Material. Wax is used in conjunction with bitumastic, elastomer, or other useful but inexpensive material for the weatherproofing and waterproofing of building materials, such as brick,

cement, asbestos-cement, stone, tile, terra cotta, and wood. The composition used must take care of the discoloration that results by the efflorescence if salts dissolved out of the building material. Certain waterproofing compositions are made to apply by brush or spray in the liquid form. Such compositions are of either a solvent, or an aqueous emulsion type.

Examples of the solvent type are (a) Chinawood oil 22, *paraffine* (122/124°F) 13, japan dryer 0.1, and solvent naphtha 64.9 parts; (b) paraffine 13, cracking oil tar 15, and solvent naphtha 65 parts[11]. An example of the aqueous emulsion type suitable for making asbestos-cement building boards water-repellent is that of Buckmann, Jr. and Rendall[20a]. It is prepared by heating to 88°C (190°F) a mixture of stearic acid 24, yellow *carnauba wax* 2.8, polybutene (m. wt. 940) 10, morpholine 3.5, stronger ammonium hydroxide (28° Bé) 4 parts, and enough water to bring the water content to 94 parts. For treatment of the board, 1 part of aqueous emulsion is mixed with titanium oxide 0.25, and water 24 parts. Polybutene of somewhat higher or lower molar weight than 940 can also be used.

Coquina Tile. A nonslip cement for the manufacture of tile has been proposed by Johannes[94]. The composition consists of coquina (50 mesh) 50, cement 13, alumina abrasives (60 mesh) 36, and *calcium stearate* (containing anhydrous silicate of 140–750 mesh) 1 part. The cement used may be "High Early," "Lumnite," standard, Portland, or white. The stearate is mixed with the water used for making the pouring mixture. Mixing is done in a cement mixer and the material then poured into forms. It is claimed that the finished material has a comparitive strength of 8000 lb/sq in., and water absorption of less than 2 per cent. It has a coefficient of static friction on leather or rubber of 0.50–0.70. The material is intended for use as tile, cover base, safety treads, shower curbs, thresholds, etc.

Wax-stone Silos. Waxed mineral staves for use in the construction of silos to hold green fodder and the like, are manufactured by pouring into forms of curved shape a concrete material consisting of cement, sand, wax, and water. The staves are of interlocking pattern to permit fast construction of the silo. The wax is a *crude scale paraffin* of 124/126°F melting point. Warm water is used in the concrete mixer so that the wax will become fluid. After the concrete has set and seasoned, the staves are shipped to the place of construction of the silo. When the silo is completed it is spray-waxed on the inside with a molten wax consisting of *paraffin* and a cheap *microcrystalline wax*, in the proportion of 1 to 2 respectively. The outside can be similarly waxed to make it thoroughly water-repellent and weatherproof. About 26,000 of such silos were constructed on the Atlantic Seaboard in 1949.

Asbestos Shingles. The Franklin Research Company, Philadelphia, Pa., have prepared wax emulsions for application to asbestos shingles to

make them more resistant to weather and repellent to water. Gaskets for soil pipes receive a treatment of wax.

Heat and Sound Insulation. Multi-ply pads or bats of heat and sound insulation, according to Fourness and Voightman[62a], can be made by uniting sheets of thin crepe cellulosic tissue by an adhesive consisting of a mixture of equal parts of asphalt (270–400°F m.p.) and *paraffin wax*.

Wax Vehicle for Glass Colors. Vehicles for glass colors have been disclosed by Jessen[92a] to be of the following compositions: (a) wax 60–85, ethylcellulose 3–10, rosin or rosin derivative 5–25, and phosphorated tall oil 5–10 parts; (b) stearic acid 30–60, hydrogenated rosin 15–20, "polypale" rosin 10–30, ethyl cellulose 0.1–10, and stearyl acid phosphate 2–7 parts. The wax employed should melt between 120 and 212°F, and can be selected from a group of waxes which includes *carnauba*, *paraffin*, *microcrystalline*, *spermaceti*, and *beeswax*.

Protective Wax Coatings on Aircraft. *Beeswax* is one of the first waxes to be reported as useful as a protective coating on airplanes. *Ouricury wax* has been used in the finishing of bombing and fighting planes on account of the high polished surfaces that can be produced with it, so that they are resistant to air friction, and to wetting or condensation. *Castorwax* has been reported as of value for waterproofing and air breaking of airplane wings. A blend of *beeswax* 20, "*A-C Polyethylene* #6" 20, and *paraffin wax* 60 parts, produces a high polished surface coherent to metal, and of good wear resistance as a protective coating.

Trusler's patented wax spray[164a] for airplane use consists of 4 parts of wax exemplified by a montanic acid ester of ethylene glycol, added to 100 parts of a petroleum solvent (flash point between 50–90°C). It is desirable to have 12.5 per cent of the wax in solution and the balance in suspension. For automobile use the ratio is 2 parts wax to 98 parts solvent, with 20 per cent of the wax in actual solution and the balance in suspension.

Wax in Flake Metal Powders. Aluminum flake powders are produced by comminuting aluminum foil scrap in ball mills in preference to the older stamping process. For any given size mesh the covering capacity of the ball-milled powder is far greater than that of the stamped product. Standard lining ball-milled aluminum flake powders show 61 per cent passing through a 325-mesh sieve. Standard lining stamped powders show only 21 per cent finer than 325 mesh.

In the past the fundamental way of making metallic powders for paint and like uses was to stamp the pieces of aluminum gold bronze alloy, or other metal, so that they would flow into flake-like particles, and the pressure would burnish and enhance the luster. Flake metal powders include aluminum (bright), zinc flake, stainless steel (18:8), flake nickel, flake silver, flake copper, and gold bronze (copper 69, zinc 30, aluminum 1 part).

As customarily carried out, the stamping resolves itself into a process of hammering the metal, such as aluminum, under mechanical stamps. This requires a suitable lubricant. The best lubricant in the past appears to have been *stearic acid*. The stamping of flake against flake seems to assist in shearing the larger flakes into smaller ones. The final operation is a polishing one in a cylindrical drum with a series of brushes bearing lightly against the inner surface. Stearic acid here again is used as a lubricant.

Metallic powders may be made tarnishproof by treating them in a hot solution of a solid synthetic polymer-wax such as *"A-C Polyethylene #7"* in an organic solvent, followed by cooling the mixture, removing the solvent, and dispersing the coated metallic particles in alkyd resin or suitable varnish material, avoiding the use of a solvent in which polymer-wax is soluble.

Waterproofing Coal Pellets. Pelletized fuel is commercially prepared by extruding silts of semibituminous or other coal. Extruded pellets normally contain 13–20 per cent moisture and are weak in strength. They can be safely handled and piled after drying to 10 per cent or less of moisture. The binderless pellets are not waterproof, but can be made so by the addition of tars of waxes to the silts. Waste wax of almost any kind will meet the need. Pellets can be produced in diameters up to at least 1 inch and up to 4 inches long.

Moldproofing Agents. Fungicides for fungusproofing materials in which wax can be used as a constituent are salicylanilide, *p*-nitrophenol, and 3,5-dinitro-*o*-cresol. For example, such fungicides when mixed with *paraffin wax* have been used for moldproofing glue-glycerol-bonded cork. Berk[15a] found that when the fungicides are mixed with 5 per cent of wax, and then dissolved in a solvent, such as isopropyl alcohol plus Stoddard solvent, and then applied to the composition cork in concentrations of 2 to 5 grams per 100 ml of solvent, they are effective against *A. niger*, *C. globosum*, *Penicillium* spp., and *Trichoderma* spp. At the Frankford Arsenal, Philadelphia, Pa.[15a], it was found that a 10-minute immersion of the cork gasket in the treating solution is primarily a surface treatment. Almost complete protection was afforded by 2 per cent *p*-nitrophenol plus 5 per cent *paraffin wax* or 5 per cent *aluminum stearate*, 1 per cent *p*-nitrophenol plus 2 per cent salicylanilide, and 1.8 per cent 3,5-dinitro-*o*-cresol. The paraffin wax increases the tenacity or resistance to weathering of the chemical protectant.

Insecticide Spray Emulsions. Dimethyl phthallate has been used in an anti-midge emulsion developed for the Department of Health, Scotland. The formulation comprises a mixture of *"Lanette Wax SX,"* triethanolamine, oleic acid, dimethyl phthallate, and water. Insecticide spray emulsions for plants, however, are preferably prepared with a fatty acid emulsifying agent of a very low iodine number in order to avoid browning of foliage.

A repellent cream for use against mosquitoes, chiggers, and black flies comprises 2-ethyl-1,3-hexanediol, *glyceryl monostearate*, *cetyl alcohol*, *lanolin*, light mineral oil, "Veegum," water, glycerol, triethanolamine, and preservative.

References

1. Abramowitz, W. L., *Modern Packaging*, **1949**, No. 6, 159–162.
2. Abrams, A., *et al.* (Marathon Paper Mills Co.), Canadian Patent 369,241 (1937).
3. ——, and Forcey, G. W., U. S. Patent 2,142,039 (1938).
4. ——, and Wagner, C. L., U. S. Patent 2,266,700 (1941).
5. ——, and ——, German Patent 702,867 (1941).
6. Adams, E. W., and MacLaren, F. H., U. S. Patent 2,127,668 (1939).
7. Aktiebolaget Lacjjus, German Patent 249,592 (1911).

7a. Alcock, R. S., and King, J., *J. Sci. Food Agr.*, **1**, 14–17 (1950).

7b. Alikonis, J. J., and Farrell, K. T., *Food Technol.*, **5**, No. 7, 228–290 (1951).

8. Andes, L. E., *Rev. Fett- u. Harz-Ind.*, **16**, 83–84 (1909).
9. Andrews, A. T., U. S. Patent 2,158,565 (1939).

9a. Anon., *Drug & Cosmetic Ind.*, **68**, 6, 769 (1951).

9b. Anon., *Soap & Sanit. Chemicals*, **27**, No. 11, 38–41 (1951).

9c. Anon., *Modern Packaging*, **27**, No. 5, 96–97, 209–210 (1954).

10. Aylsworth, J. W., U. S. Patent 1,283,450 (1919).
11. Baldeschwieler, E. L., and Gaylor, P. U. S. Patent 2,199,193 (1940).

11a. Barta, E. J., and Lowe, E., *Western Canner and Packer*, **41**, No. 12, 51 (1949).

11b. Bartels, H. J. M., and van der Welen, P., *Pharm. Weekblad*, **48**, 1021–1025 (1911).

12. Beckers, W., U. S. Patent 1,094,360 (1914).
13. Beiersdorf, Ltd., and Moore, F. G., British Patent 454,759 (1936).
14. Beklemisheva, N. A., *et al.*, Russian Patent 54,984 (1939).
15. Bennett, H., "Practical Emulsions," Brooklyn, N. Y., Chemical Publishing Co., Inc., 1943.

15a. Berk, S., *Ind. Eng. Chem.*, **40**, 262 (1948).

16. Bolton, E. S., "Wax Portraits and Silhouettes," sponsored by the Mass. Soc. of the Colonial Dames of America, New York, Houghton Mifflin Co., 1914.

16a. Borden, Jr., G. C., and Wolper, P. K., *Modern Packaging*, **23**, No. 12, 111–117 (1950).

17. Bowen, F. E. W., British Patent 21,481 (1903).
18. Braude, F., "Adhesives," Brooklyn, N. Y., Chemical Publishing Co., Inc., 1943.
19. Brower, P. V., U. S. Patent 2,138,836 (1938).
20. Bryant, J. D., U. S. Patent 987,042 (1911).

20a. Buckman, Jr., A. F., and Rendall, M. M., U. S. Patent 2,504,920 (1950).

21. Burrows, F. R., and Burrows, J. G., British Patent 11,582 (1914).
22. Burrows, J. (Port Arthur, Ontario), U. S. Patent 968,919 (1910).
23. Butcosk, R. A. (Shell Development Co.), U. S. Patent 2,445,936 (1948).
24. Cable, A. J. (West Australian Paper Bag Co., Ltd.), Australian Patent 113,451 (1941).
25. Calvert, W. C., U. S. Patents 1,846,309 and 1,846,790 (1932).
26. Carmody, W. H., U. S. Patent 2,302,644 (1943).
27. Casparis, P., and Meyer, E. W., *Pharm. Acta Helv.*, **10**, 163–182 (1935).
28. Charch, W. H. (E. I. du Pont de Nemours & Co., Inc.), U. S. Patent 2,147,629 (1939).

28a. ——, and Hershberger, A., U. S. Patent 2,077,396 (1937).
29. Chas. H. Phillips Chemical Co., French Patent 787,532 (1935).
30. Clare, I. C., U. S. Patent 2,529,282 (1950).
30a. Clarke, C. D., "Molding and Casting," Baltimore, Md., John D. Lucas Co., 1938.
31. Clayton, W., *et al.* (to Crosse & Blackwell, Ltd.), U. S. Patent 2,215,144 (1941).
32. Cohoe, W. P. (to American Chicle Co.), U. S. Patent 2,444,871 (1948).
33. Cole, J., U. S. Patent 2,101,241 (1937).
34. Coleman, L. V. (American Museum of Natural History), Guide Leaflet Series No. 54, pp. 3–16, 1922.
34a. Cook, A. A., *et al.*, U. S. Patent 2,603,576 (1952).
34b. Copley, C. J. (ed.), *Oil-Power*, **25**, No. 4, 6–7 (1950).
35. Cordray, J. W., U. S. Patent 1,054,751 (1913).
35a. Corkery, F. W., and Burroughs, S. G., U. S. Patent 2,319,389, Reissued Feb. 22, 1943.
36. Cornwell, R. T. K., U. S. Patent 2,121,023 (1938).
37. Cothran, C. D., U. S. Patent 2,261,229 (1942).
38. ——, U. S. Patent 2,329,513 (1943).
39. Crass, Jr., M. F., *Chem. Ind.*, **48**, 424–433; *ibid.*, 575–579 (1941).
40. Davidsohn, A., and Davidsohn, I., "Shoe Creams and Polishing Waxes," New York, Chemical Publishing Co., Inc., 1939.
41. Davis, C. C., and Blake, J. T., "The Chemistry and Technology of Rubber," New York, Reinhold Publishing Corp., 1937.
42. Davis, H. S., U. S. Patent 1,815,022 (1931).
42a. Davis, C., and Thacker, N. A. (To National Cash Register Co.), U. S. Patent 2,646,367 (1953).
43. Dearborn, F. E., U. S. Patent 2,427,717 (1947).
43a. Decepoli, C., U. S. Patents 2,486,826 and 2,486,827 (1949).
43b. De Coste, J. B., U. S. Patent 2,532,699 (1950).
44. Deguide, H., U. S. Patent 2,126,096 (1938).
45. De Keghal, M., *Chem. Ind.*, **29**, 107–112 (1932).
45a. Delmonte, J., *Modern Plastics*, **28**, 64–67 (1951).
46. Diggs, S. H., Beard, R. E., and Page, Jr., J. M., U. S. Patent 2,050,428 (1936).
47. Dixson, W. H., "The Match Industry: Its Origin and Development," London, Sir Isaac Pitman & Sons, Ltd., 1937.
47a. Dodd, H. (Imperial Chemical Industries, Ltd. Great Britain), U. S. Patent 2,124,888 (1938).
48. Dodge, L. L., U. S. Patent 2,319,116 (1943).
49. Dr. Fuchs and Co., British Patent 245,313 (1925).
50. Dutton, W. C., U. S. Patent 2,198,991 (1940).
51. Eagle Pencil Co., Canadian Patent 357,438 (1936).
51a. Easton, N. R., Cross, S. T., *et al.*, *Food Technol.*, **6**, No. 1, 21–25 (1952).
52. Eberlin, L. W., and Burgess, A. M., *J. Ind. Eng. Chem.*, **19**, 87 (1927).
52a. Ellern, H. (to Universal Match Corp.), U. S. Patent 2,495,575 (1950).
53. Ellis, C., "The Chemistry of the Petroleum Derivatives," Vol. 2, New York, Reinhold Publishing Corp., 1937.
54. ——, U. S. Patent 1,145,980 (1915).
54a. ——, U. S. Patent 1,189,804 (1916).
55. ——, U. S. Patent 1,276,507 and 1,276,508 (1918).
56. Ennis, E. C., U. S. Patent 2,187,734 (1940).
57. Fairburn, W. A., U. S. Patent Reissue 13,638 (1913).

58. Fassbender, H. (to Milprint, Inc.), U. S. Patent 2,302,200 (1942).
59. Feagin, Roy C., U. S. Patent 2,439,488 (1943).
60. Flint, G. W., U. S. Patent 2,045,455 (1936).
61. Flint, J. E., U. S. Patent 2,184,182 (1939).
62. Forrest, C. N., U. S. Patent 877,883 (1908).
62a. Fourness, C. A., and Voigtman, E. H., U. S. Patent 2,292,513 (1943).
63. Freeman, H. G., *Pharm. J.*, **120**, 412 (1928).
64. Frolich, P. K., U. S. Patent 2,322,012 (1943).
65. Fuld, M., *Soap*, **15**, 95–97, 113 (1939).
66. Gargen, O. F., and Ernst, C. J., U. S. Patent 2,125,237 (1938).
67. Geller, L. W., *Oil & Soap*, **12**, 263–264 (1935).
68. Glickman, C. A., *Chem. Ind.*, **45**, 301 (1939).
68a. ——, *Soap Sanit. Chemicals*, **14**, No. 10, 86–88, 101, 103; No. 11, 95, 97, 99, 117 (1938).
69. ——, *Chem. Ind.*, **53**, 496 (1943).
70. Golden, E. H., *J. Am. Dental Assoc.*, (June 1926).
71. Goldreich, S., *et al.*, British Patent 123,775 (1917).
72. Goodman, H., and Suess, A., *Urol. Cutaneous Rev.*, **42**, 909–910 (1938); [*Chem. Abstracts*, **33**, 1443 (1939)].
73. Gradnich, B., *Bull. chim. farm.* **87**, 55–56 (1948).
73a. Grate, L. G., U. S. Patent 2,548,970 (1951).
73b. Greenstreet, O. P., U. S. Patent 2,510,816 (1950).
74. Griffith, R. (to National Oil Products Co.), U. S. Patent 2,288,351 (1942).
75. Groat, R. A., *Science*, **93**, 2413 p. 311 (1941).
76. Haller, M. H., *Proc. Am. Soc. Hort. Sci.*, **50**, 325–329 (1947).
77. Halpern, A., and Zopf, L. C., *J. Am. Pharm. Assoc., Sci. Ed.*, **36**, 101–104 (1947).
78. Handy, J. O., U. S. Patent 2,424,952 (1947).
78a. Happoldt, W. S., Jr., and Stockfleth, A. (to E. I. du Pont de Nemours & Co., Inc.), U. S. Patent 2,448,799 (1948).
79. Harper, F., "Military Ski Manual," Harrisburg, Pa., Military Publishing Co., 1943.
80. Harris, H. A., U. S. Patent 1,145,365 (1915).
81. Harry, R. G., "Modern Cosmeticology," New York, Chemical Publishing Co., 1940.
82. Hattori, S., U. S. Patent 1,292,404 (1919).
82a. Hawley, T. G., *et al.*, U. S. Patent 2,483,701 (1949).
83. Head, R., U. S. Patent 1,358,949 (1921).
83a. Hinds, Wm. E., U. S. Patent 2,487,336 (1949).
84. Houston, J. F., U. S. Patent 1,277,215 (1918).
85. Houston, R., and Kale, E. W., *Western Canner and Packer*, **41**, No. 13, 57, 60 (1950).
86. Howe, C. C., and Libby, S. W., U. S. Patent 1,457,169 (1923).
87. Huber, W., U. S. Patent 2,322,445 (1945).
88. Hughes, C. M. C., and Nathan, C., British Patent 14,149 (1911).
89. Hunter, J. H., U. S. Patent 2,240,300 (1941).
90. Ingle, J. D., U. S. Patent 2,292,323 (1942).
91. ——, and Mink, L. D., U. S. Patent 2,299,951 (1942).
92. ——, and ——, U. S. Patent 2,329,470 (1943).
92a. Ivanovszky, Leo, *Chem. Listy*, **26**, 331–332, 332–335 (1932); cf. *Chem. Abstracts* **26**, 6170 (1932).
93. Jasinski, J. v., German Patent 273,346 (1913).

93a. Jessen, C. C. (to E. I. du Pont de Nemours & Co., Inc.), U. S. Patents 2,607,701 and 2,607,702 (1952).
94. Johannes, Jr., D. B., U. S. Patent 2,411,213 (1946).
95. J. Spicer & Sons, British Patents 139,533 and 139,534 (1918).
96. Kalish, J., *Drug. & Cosmetic Ind.*, **45**, 678–680 (1939).
97. Kallander, E. L., and Asnes, B., U. S. Patent 2,233,090 (1941).
98. Kazda, J., U. S. Patent 1,602,437 (1926).
99. Kellermann, A., U. S. Patent 2,262,238 (1941).
100. Kelley, W. Carl, *J. Am. Pharm. Assoc., Sci. Ed.*, **37**, 253–254 (1948).
100a. Kirk, R. E., and Othmer, D. F., "Encyclopedia of Chemical Technology," Vol. 6, pp. 66–68, New York, The Interscience Encyclopedia Inc., 1951.
100b. Kjellstrand, A. G. (to Interchemical Corp., N. Y.), U. S. Patent 2,322,367 (1943).
100c. Knaggs, N. S., "Adventures in Man's First Plastic," Reinhold Publishing Corp., 1947.
101. Knoepfler, G., U. S. Patent 1,084,091 (1914).
101a. Knuth, E. H. (to Diamond Alkali Co.), U. S. Patent 2,640,366 (1953).
102. Langenhagen, G., U. S. Patent 406,102 (1889).
103. Laufer, R. E., U. S. Patent 2,227,787 (1941).
104. Lee, J. A., and Lowry, H. H., *J. Ind. Eng. Chem.*, **19**, 304 (1927).
105. Lesser, M. A., *Drug. & Cosmetic Ind.*, **49**, 151–154, 161 (1941).
106. Libovitz, H., *et al.* (Allegro Co.), U. S. Patent 2,129,377 (1938).
107. Lieber, E., U. S. Patent 2,281,941 (1942).
108. Lovell, S. P., U. S. Patent 2,258,376 (1942).
108a. ——, U. S. Patent 2,329,201 (1944).
108b. ——, and Straw, H. H., U. S. Patent 2,346,136 (1944).
109. Lowden, W. P., U. S. Patents 2,456,717 (1948) and 2,486,487 (1949).
109a. Luciani, J., French Patent 380,963 (1906).
110. Lux, H., *Allgem. Oel- u. Fett-Ztg.*, **32**, 153–157 (1935).
111. Macek, T. J., U. S. Patent 2,493,202 (1950).
111a. Mack, W. B., and Janer, J. R., *Food Research*, **7**, 38–47 (1942).
112. Majumdar, V. P., *Science and Culture*, **7**, 270–271 (1941).
112a. Marran, J. S., U. S. Patent 2,242,313 (1941).
113. Martin, G., "Animal, Vegetable Oils, Fats, and Waxes," London, Crosby, Lockwood & Sons, 1920.
114. Matumoto, T., *Repts. Chem. Research, Prefectural, Inst. Advancement Ind.*, No. 3, 14–15 (1940); [*Chem. Abstracts*, **35**, 7652 (1941)].
115. Mayer, C. W., U. S. Patent 1,043,021 (1912).
115a. McClenahan, W. S., and Nelson, H. A. (to Chesebrough Mfg. Co., Consolidated), U. S. Patent 2,523,316 (1950).
116. Meyer, E., *Drug. & Cosmetic Ind.*, **49**, 270–271 (1941).
117. Millar, C. C. H., British Patent 119,477 (1916).
118. Moore, A. E., *Chem. Ind.*, **66**, 385–386, 388–392 (1950).
118a. Moore, J. E. (to Monsanto Chemical Co.), U. S. Patent 2,500,427 (1950).
119. Moran, Robt. C., *et al.*, U. S. Patent 2,322,093 (1943).
119a. Morton, J. L., and George, H. O. (To International Business Machines Corp.), U. S. Patent 2,562,676 (1951).
120. Murphy, T. F., U. S. Patent 2,377,172 (1945).
121. Navarre, M. G., de, and Mill, R. J., "The Chemistry and Manufacture of Cosmetics," New York, D. Van Nostrand Co., Inc., 1941.
122. Neidich, S. A., U. S. Patent 2,236,602 (1941).

123. Newberg, R. G., *Modern Packaging*, **23**, 121–124, 172 (1950).
124. Newburger, S. H., *J. Assoc. Offic. Agr. Chemists*, **30**, 683–690 (1947).
125. Olsen, A. B., *Chem. Ind.*, **59**, 70–71 (1946).
125a. Olshausen, J., *et al.*, *Brewers Digest*, **19**, No. 7, 40–41, 39T-4T (1944).
125b. Osol, A., and Farrar, G. E., "The Dispensatory of the United States of America," 24th Ed., Philadelphia, Pa., J. P. Lippincott Co., 1947.
126. Padgett, F. W., U. S. Patent 2,282,375 (1942).
127. Palmer, W. H., French Patent 394,833 (1908).
128. Parker, C. J., U. S. Patent 2,073,648 (1937).
128a. Parker, M. E., *Food Ind.*, **22**, 57–59 (1950).
129. Pearsall, D. E., U. S. Patent 1,917,540 (1933).
130. Pease, F. N., and McDonnell, M. E., U. S. Patent 972,638 (1910).
131. Pedersen, J. D., U. S. Patent 1,780,566 (1930).
132. Pekkering, J. J., and Hintzer, H. M. R., *Chem. Weekblad* (Sept. 24, 1949); [cf. *Food Ind.*, **22**, No. 2, 128 (1950)].
132a. Pentzer, W. T., *et al.*, *U. S. Dept. Agr., Tech. Bull. No. 730* (*re* California Cantaloups), pp. 1–74 (July 1940).
133. Pfaff, K., *Reichsamt. Wirtschaftausbau*, *Chem. Ber.*, PB 52021 1198-12-5 (1942).
134. Pirelli-General Cable Works, Ltd., and Ashford, B. O., British Patent 574,045 (1946).
135. Prince, Jr., L. M., U. S. Patent 2,441,842 (1948).
136. Proell, W. A., U. S. Patent 2,261,451 (1942).
137. Rabak, W. (Western Regional Research Lab., Albany, Calif.), *Canner*, **110**, No. 19, 11–12 (1950).
137a. Rau, K., U. S. Patent 1,863,416 (1932).
138. Redgrove, H. S., *Am. Perfumer Essent. Oil Rev.*, **38**, No. 3, 35–36 (1939).
139. Reed, R. K., U. S. Patent 2,158,524 (1939).
140. Reiff, O. K., U. S. Patent 2,191,499 (1940).
140a. ——, *et al.* (to Socony Vacuum Oil Co., Inc.), U. S. Patent 2,475,916 (1949).
141. Reifsnyder, J. D., U. S. Patents 1,602,835 (1926) and 1,703,638 (1929).
141a. Rogers, L. F., and Ebert, M. S., U. S. Patent 2,597,378 (1952).
142. Rosen, H. R., U. S. Patent 2,089,506 (1937).
143. Sajak, E., U. S. Patent 1,922,007 (1935).
144. Schilling, A. A., and Latham, G. H. (Remington Arms Co.), U. S. Patent 2,286,112 (1942).
145. Schlegel, J. W., and Lang, L., U. S. Patent 2,320,831 (1943).
145a. Schneider, H. G., Young, D. W., and Rocca, J. P. (to Standard Oil Development Co.) U. S. Patent 2,577,816 (1851).
145b. Schreffler, C. B., *Wines & Vines*, p. 29 (June 1950).
146. Schuh, C. H., U. S. Patent 2,221,956 (1940).
147. Schur, M. O., Canadian Patent 406,395 (1942).
147a. Seil, H. A., and Cole, H., U. S. Patent 2,499,004 (1950).
148. Shapiro, A., U. S. Patent 2,153,161 (1939).
149. Sharma, J. N. (Food Machinery Corp.), U. S. Patent 2,133,404 (1939).
150. ——, U. S. Patent 2,153,487 (1939).
150a. ——, U. S. Patent 2,290,452 (1942).
151. Shearon, Jr., W. H., and Hoiberg, A. J., *J. Ind. Eng. Chem.*, **41**, 2676–2679 (1949).
152. Shuger, L. W., U. S. Patent 2,081,073 (1937).
153. Skinner, E. W., "The Science of Dental Materials," Philadelphia and London, W. B. Saunders Co., 1943.
153a. Slater, L. E., *Food Eng.*, **23**, No. 10, 92–93 (1951).

154. Smith, H. W., U. S. Patent 1,131,432 (1915).
155. Sorenson, E., U. S. Patent 1,709,498 (1929).
156. Standage, H. C., "Sealing Waxes, Wafers, and other Adhesives," New York, D. Van Nostrand Co., Inc., 1903.
157. Standard Oil Co., U. S. A., German Patent 357,507 (1905).
158. Standard Oil Development Co., British Patent 584,800 (1947).
159. Swett, A. P., U. S. Patent 2,309,023 (1943).
160. Thiele, F. A., *Pharm. Weekblad*, **79**, 354 (1942); [*Drug & Cosmetic Ind.*, **53**, 553 (1943)].
161. Thomas, G. C. (to The Lummus Co.) U. S. Patent 2,290,393 (1942).
162. Thomas, R., and Whitham, H., U. S. Patent 2,366,759 (1945).
163. Thompson, H. P., British Patent 13,975 (1911).
163a. Towner, J. C. (to Hardie Trading Pty. Ltd.), Australian Patent 116,036 (1942).
164. Tressler, D. K., *Fruit Products J.*, **24**, 4, 107 (1945).
164a. Trusler, R. B., U. S. Patent 2,596,829 (1952).
165. United States Pharmacopoeia, XIII, Printed by Mack Printing Co., Easton, Pa., Agent, 1947.
165a. *Ibid.*, XIV Revision, 1950.
166. Van Horn, H. T., *Am. Ceram. Soc. Bull.*, **26**, 229–231 (1947).
167. Van Riel, Jr., and Van der Wielen, P., *Pharm. Weekblad*, **49**, 566–568 (1912).
167a. Veneklasen, P. S., and Watson, N. A., U. S. Patent 2,451,186 (1948).
168. Wade, S. E., British Patent 312,200 (1927).
169. Walker, P. H., and Steele, L. L., *U. S. Bur. Standards Tech. Paper No. 176* (1920).
170. Walton, B., U. S. Patent 1,999,160 and 1,999,161 (1935).
171. Warth, A. H., Jr., previously unpublished data.
171a. Wassermann, R., U. S. Patent 2,309,488 (1943).
171b. Weihe, Jr., F. A. (to McAleer Mfg. Co.), U. S. Patent 2,214,263 (1940).
171c. Welch, T. H., *Soap Sanit. Chemicals*, **28**, No. 1, 117–121 (1952).
172. Wells, F. B., U. S. Patent 2,317,159 (1943).
173. Weil, M. A., U. S. Patent 2,317,159 (1943).
173a. Weston, C. C., U. S. Patent 2,525,984 (1950).
174. Wiertelak, J., and Czarnecki, J., *J. Ind. Eng. Chem.*, **27**, 543 (1935).
175. Wilson, J. M., and Bacon, C. V., U. S. Patents 1,167,462 (1916) and 1,167,469 (1916).
176. Wolfe, H. J., "Manufacture of Printing and Lithographic Inks," New York, MacNair-Dorland Co., 1933.
177. Worden, E. C., "Technology of Cellulose Esters," Vol. 8, pp. 2890–2893, New York, D. Van Nostrand Co., Inc., 1916.
178. Worgan, G., "The Art of Modelling Flowers in Wax," Brooklyn, N. Y., H. H. Dickinson, 1867.
179. Worton, A. G., *et al.*, *J. Am. Pharm. Assoc.*, **27**, 21 (1938).

Appendix

Tables of Physical Constants of Waxes

Viscosity and Specific Gravity of Waxes at Changing Temperatures

Wax	Temperature (°F)	Viscosity Saybolt Universal (sec)	Specific Gravity T°/15°C
Paraffin	60	—	0.9086
m. 128–130°F	140	50.6	0.8105
	180	42.5	0.7970
	210	39.0	0.7875
	250	35.8	0.7725
Ozocerite (JAA)	180	53.8	0.8120
m. 167°F	220	44.6	0.7965
	250	41.7	0.7870
Beeswax, white	160	119.0	0.8670
m. 148°F	205	73.7	0.8505
	250	54.6	0.8345
Beeswax, yellow	165	103.9	0.8650
m. 146°F	205	69.4	0.8490
	250	54.0	0.8350
Ceresin, artificial	180	42.1	0.7985
m. 166°F	220	37.9	0.7855
	250	36.3	0.7750
Ozocerite, commercial	170	55.9	0.8120
m. 161°F	210	46.1	0.8010
	240	42.5	0.7870
	250	41.7	0.7840

Viscosities—Saybolt Standard Universal—Seconds

Wax	190°F	200°F	210°F	230°F	260°F	Flow
Beeswax, white	87.0	77.0	70.7	61.0	54.6	sluggish
Ceresin, artificial	40.5	39.7	39.0	37.0	36.6	fast
Microcrystalline, amber 170/175°F ASTM	93.0	86.0	79.5	68.0	58.8	sluggish
Ozocerite, bleached	51.8	49.0	47.0	44.0	41.6	slow
Paraffin, commercial						
128/130°F AMP	41.3	41.3	39.0	37.3	35.2	fast
134/136°F AMP	40.4	39.3	38.2	36.7	34.7	fast
143/145°F AMP	43.9	42.1	40.4	38.4	36.3	fast
152/154°F AMP	48.0	45.8	44.0	41.2	38.2	fast

Kinematic Viscosity—Centistokes (cks)

Wax	At 70°C	At 80°C	At 99°C
"Arwax S Polymer Concentrate 813-4"	—	—	45
"Aristowax"			
149/151°F ASTM	—	—	5.5
160/165°F ASTM	—	—	7.5
Beeswax			
Yellow	—	17.3	12.1
White	—	19.6	12.9
Candelilla	—	—	17.0
Carnauba	—	—	33
Ceresin, lubricating	—	—	4.0
Ceresin, petroleum (hard, m. 180°F)	—	—	10.0
Douglasfir	—	—	18.4
Fischer-Tropsch			
"FT 200"	—	—	7.4 (130°C)
"FT 300"	—	—	10.7 (130°C)
Jojoba oil	—	—	6.54 (Wells)
Lauric acid, m. 44°C	5.1	—	—
Microcrystalline (A) soft			
140/150°F ASTM	—	—	10.2
150/155°F ASTM	—	—	12.6
160/165°F ASTM	—	—	15.6
175/180°F ASTM	—	—	19.6
Microcrystalline (B) hard			
160/165°F ASTM	—	—	9.0
165/170°F ASTM	—	—	9.2
170/175°F ASTM	—	—	12.6
185/190°F ASTM (tank bottom)	—	18.5 (90°C)	14.5
190/195°F ASTM	—	—	18.4
195/200°F ASTM	—	—	22.0

Wax	At 70°C	At 80°C	At 99°C
Microcrystalline (C) medium hard			
155/160°F ASTM, m. 157°F	—	—	9.0
160/165°F ASTM	—	—	10.6
170/175°F ASTM	—	—	14.0
180/185°F ASTM	—	—	17.0
185/190°F ASTM, m. 187°F	—	—	17.9
Microcrystalline (D) paraffin-like			
140/145°F ASTM	—	—	6.0
150/155°F ASTM	—	—	7.4
160/165°F ASTM	—	—	8.0
Montan	—	—	53.2
Myristic acid, m. 54°C	6.8	—	—
Ozocerite, "JAA," m. 167°F	—	—	6.6
Ozocerite, m. 161°F	—	—	5.8
Palmitic acid, m. 63°C	9.2	—	—
Paraffin			
Scale wax, m. 102°F	—	—	3.7
118/120°F AMP	—	—	3.9
124/126°F AMP	5.4	—	—
128/130°F AMP	5.9	4.8	4.0
132/134°F AMP	—	—	4.1
134/136°F AMP (hard)	5.8	4.6	3.6
143/145°F AMP (hard)	7.2	6.4	4.2
152/154°F AMP	—	7.9	5.6
163/165°F AMP	—	—	7.4
Polyethylene glycol			
500–600 mol. wt.	—	—	13–18
1300–3700 mol. wt.	—	—	25–32
3000–3700 mol. wt.	—	—	75–85
Stearic acid, m. 70°C	11.3–11.9	—	—
Stearic acid, USP, m. 57°C	6.6	—	—
"Utahwax" (American ozocerite)	—	—	20 (95°C)
Wax Blends			
% Paraffine / % Carnauba			
100 / 0	6.5 (65°C)	5.0	3.55
98 / 2	—	5.2	3.6
95 / 5	14.7 (65°C)	5.9	3.8
90 / 10	—	—	4.8
80 / 20	—	—	5.7
70 / 30	—	—	6.7
0 / 100	—	—	34.0
% Paraffine / % Butyl Rubber			
100 / 0	6.5	5.0	3.55
99 / 1	—	—	6.3
98 / 2	—	—	10.2
97 / 3	—	—	16.3
96 / 4	—	—	25.5

Kinematic Viscosity—cks at 99°C (210°F)

% Paraffine 124/126	% Polyethylene Mol. Wt. 2000	Cks at 99°C	% Paraffine 133/135	% Polyethylene Mol. Wt. 2000	Cks at 99°C
100	0	3.9	100	0	4.0
98	2	4.0	98	2	4.2
96	4	4.3	96	4	4.45
94	6	4.8	94	6	5.6
90	10	6.7	92	8	7.3
85	15	10.0	90	10	9.5

Hardness Values of Waxes (Shore Durometer)

Wax	At 4°C	At 25°C
Bayberry	85–88	71–78
Beeswax		
Yellow USP	70–75	43–50
White USP	82–87	59–66
Candelilla	100	99–100
Caranda	100	98–100
Carnauba	100	97–100
"Castorwax"	99–100	93–99
Ceanothus	98–99	93–94
Ceresin		
Cheap artificial; M.P. 145°F	73	32
"Italian White," M.P. 158°F	75–77	49–55
Imitation domestic, M.P. 165°F	83	68
Genuine (ozocerite) M.P. 167°F	77	58
Cetyl alcohol	—	68–72
Douglasfir bark	100	65
Esparto	100	96–99
Flax	100	99
"Gersthofen OP"	100	99–100
Japanwax	70–75	27–44
Laurone	85	74
Microcrystalline		
Brown-yellow, laminating, 145/150°F ASTM	36–40	71–72
White, ceresin type, 150/155°F ASTM	41–48	72–74
Amber, Oklahoma, 160/165°F ASTM	77	51–52
White, Oklahoma, 163/165°F ASTM	78	53–54
Amber, 170/175°F ASTM	79–81	62–67
Pale Yellow, 185/190°F ASTM	90	80
White, 190/200°F ASTM	86–95	80–90
Pale Yellow, 190/195°F ASTM	89	81–84
Montan, crude black	100	99
Montan, bleached yellow-white	85	78
Orange peel	99–100	92–94
Ouricury	100	100
Ozocerite, pure white	67–70	58
Palm, commercial	90	82
Palmitone	100	96

Wax	At 4°C	At 25°C
Paraffin, American		
123/125°F AMP	70–73	43–51
128/130°F AMP	75–77	55–61
133/135°F AMP	78–80	62–64
138/140°F AMP	81	66
143/145°F AMP	83	70
152/154°F AMP	85	77
160/165°F AMP	88–90	80–82
Paraffin, Asiatic		
128/130°F AMP	85	74
148/150°F AMP	88	76
"Rezowax A" (synthetic)	100	100
Shellac	90	84
Spermaceti	70	49
Stearanilide	78–82	60–70
Stearic acid		
"Neo-Fat 90%"	68–72	55
Ordinary commercial	84	76
USP	95	90
Stearone	99–100	93
Sugarcane, refined	100	98
Utah ozocerite, refined yellow	80	70
Vegetable fiber	91	85

Penetration Values of Waxes at 25°C (77°F)

(P. needle #14—5 sec penetration—100 g top wt.)

Wax	Value (mm × 10)
Bayberry	7.5
Beeswax	
Refined, ordinary	10
White, sun-bleached USP	11
Yellow, USP	17
Candelilla	1
"Cardis One," (extra hard emulsifiable)	1–2
"Cardis 320" (oxidized petroleum wax)	4–5
Carnauba	0.8–1.6
"Castorwax" (12-hydroxy stearin)	1
Ceresin	
Artificial, for lubricating	23–25.5
Artificial, ordinary	18–21
Domestic, hard, m. 185°F	8.5
Italian white, m. 158°F	15
Cetyl alcohol	19
Cotton wax	50.2 (21°C, 200 g/10 sec)
Douglasfir bark	4.5–5
"Epolene E" and "N" (polyethylene waxes)	<2.0
Esparto	1.5
Flax	3

Wax	Value (mm × 10)
Fischer-Tropsch "FT Wax 200"	3–5
Fischer-Tropsch "FT Wax 300"	0.9–1.1
"Gersthofen Wax OP"	1
Japanwax	23–36
Laurone	11.6
"Micris 777 Yellow," m. 190°F	5.0, 36 (71°F)
Orange peel	7
Ouricury	1–1.5
Ozocerite, pure white	13.5
Palmitone	4.0
Paraffin, American	
123/125	14–22 (94–130 at 38°C)
128/130	14–18 (52–112 at 38°C)
134/136	11–13 (30–45 at 38°C)
138/140	9–13 (18–24 at 38°C)
143/145	9–12 (15–22 at 38°C)
152/154	8–10 (14–19 at 38°C)
Paraffin, Asiatic	
148/150	7–7.6
Petrolatum	150–190
Shellac	4–6.5
Spermaceti	13–16
Stearic acid	
"Neo-Fat" 90% (Armour & Co.)	13
Ordinary commercial	7
USP	3
Stearone	2.1
Sugarcane, refined	1.5
"Utahwax," American ozocerite	4.3 (20°C) (38 at 60°C)
Vegetable fiber	3

Penetration Values of Microcrystalline Waxes of Low Oil Content

(0.6–5 Per Cent). Penetration at 77°F

Per Cent	160/170			170/180		180/190		190/200
Oil	(a)	(b)	(c)	(a)	(c)	(c)	(d)	(e)
4.8	35.5	25	17.1	51	13	17.3	8.8	4.2
4.0	32.5	22	16	46	12	16	8	4
3.4	30.5	20	14.7	43	11	14.5	7.5	3.5
3.0	29	19	14	41.3	10.5	14	7	3.4
2.5	—	18	13	40	9.7	13.2	6.6	3.2
2.0	—	—	12.3	—	8.5	12.5	6.3	—
0.66	—	—	—	—	—	11	5	—
0.6	—	—	—	—	—	—	—	2

Note: (a) refers to penetration values (30 plus) of a *very soft* wax of less than 5 per cent oil content; (b) penetration (20–30) of a *soft* wax; (c) penetration (10–20) of a *medium hard* wax; (d) penetration (5–10) of a *hard* wax; and (e) penetration (0.6–5) of a *very hard* wax.

Penetration Values of Microcrystalline Waxes of Medium Oil Content

(5–10 Per Cent). Penetration at 77°F

Per Cent	160/170			170/180			180/190
Oil	(a_1)	(a_2)	(b)	(a_1)	(a_2)	(c)	(c)
9.8	66	47	28	82	35.5	20	13.5
8.6	57	41	26	74	31	18.2	12.5
8.0	52	38	24.5	70	29	17.6	—
7.5	48.8	33	23.5	67	27	16.5	11.4
6.4	43	30.5	21.3	60	24	15.3	10.2
5.8	40	28	—	57	21	—	—
5.4	38	—	—	54	20.5	13.5	9.5

Note: (a_1) refers to an optimum penetration value of 50 plus of a very soft wax with an oil content of 5–10 per cent; (a_2) of a very soft wax of 30–50 penetration; (b) of a soft wax of 20–30 penetration; and (c) of a medium hard wax of 10–20 penetration.

Penetration Values of Microcrystalline Waxes of High Oil Content

(10–15 Per Cent). Penetration at 77°F

Per Cent Oil	150/160 (crude)	160/170		170/180 (crude)		190/195
	(a_1)	(a_1)	(a_2)	(a_1)	(b)	(d)
14.8	70	—	39	55	27.5	9
14.0	74	—	37	52	26	8.5
13.6	72	85	36.3	49.5	25.3	8.3
12.4	65	78	33.8	45	24	8
10.4	—	66	29.5	38	21	7

Note: (a_1) refers to an optimum penetration value of 50 plus for a very soft wax with an oil content of 10–15 per cent; (a_2) for a very soft wax of 30–50 penetration; (b) for a soft wax of 20–30 penetration; and (d) for a moderately hard wax of 5–10 penetration.

Melting Points of Waxes

Wax	Melting Point (°C)	Melting Point (°F)	Solidifying Point (°C)
Jojoba	11.2–11.8	52.1–53.2	6.7
Cay-cay, Cochin-China	—	87.8	—
Paraffin scale	35–40	95–104	—
Woolwax (anhydrous lanolin)	36–43	96.8–109.4	30–39
Ucuhuba	41–44	105.8–111.2	—
Hydrogenated coco oil	43–45	109.4–113	—
Orange skin	44–46.5	111.2–115.7	36–38.5
Spermaceti	44.4–47	112–116.6	42–42.5
Bayberry	46.7–48.8	116–120	39–43
Paraffin 118/120 AMP	47.8–48.9	118–120	—
Cetyl alcohol	48–49.3	118.4	—
Japanwax, old	48.5–49.5	119.3–121	40.5–41 (setting point 45.6–46)
Sorbitol distearate	49–51	120.2–123.8	—
"Lanette Wax"	50	122	—
"Spermafol 52"	50–52	122–125.6	—

Wax	Melting Point (°C)	Melting Point (°F)	Solidifying Point (°C)
Paraffin 123/125 AMP	51–52.2	123.8–126	50.8 (cloud point 51)
Cetyl palmitate, pure	51.6	125	
Japanwax, new	51–53	123.8–127.4	50.0
Insect wax (Ceroplastes)	52–58.5	125.6–137.3	—
Paraffin 128/130 AMP	53.5–55	128.3–131	52.8–53.4 (cloud point 53.6)
Diglycol stearate	54–59	129.2–138.2	—
Arjun, Indian	55–63	131–145.4	—
Stearic acid, flaked USP	56–57	133–135	54.4–56.6
Slop paraffin	55.5–83.3	132–182	—
"Pliowax"	55.6	132	—
Glyceryl monostearate	56–57	132.8–134.6	—
Ponderosa bark	56–60	132.8–140	—
Paraffin 133/135 AMP	56.5–57.8	133.7–136	56.1
Chinese tallow tree	56.8	134.2	—
"Carbowax Stearate" (highest m.p.)	57	134.6	—
Cetyl acetamide	58.3–59.5	137–139	—
Paraffin 138/140 AMP	59–60	138.2–140	57.4
Ceresin, artificial	59.5–71	139–140	—
Jasmine floral	60	140	56–57
Sugarcane, East Indian	60–62	140–143.6	—
Ghedda	60.4–66.4	140.7–151.5	60
Rose floral	61	141.8	—
Flax	61–72	141.8–161.6	—
Hydrogenated cottonseed oil	62–63	143.6–145.4	—
Douglasfir bark, ether extracted	62–63	143.6–145.4	—
Beeswax, yellow ordinary	62–66	143.6–152.8	60–63.5
Beeswax, white USP	62.5–64.7	144.5–148.5	61–63.5
Paraffin, American 143/145 AMP	62.8	145	61.1
Beeswax, yellow USP	63–64.2	145.2–147.6	61–63
Paraffin, Asiatic 148/150 AMP	63.3	146	—
Cranberry skin, cold hexane extracted	64.0	147.2	—
Beeswax, African	64–65	147.2–149	61–62
Ozocerite, commercial bleached	65–70	149–158	60.5–64
Cotton, true	66–73	150.8–163.4	—
Laurone, commercial	66.5–68	151.7–154.4	—
Stearic acid, commercially pure	67	152.6	—
"Karawax"	67–70	152.6–158	—
Hemp, common	67–74	152.6–165	—
Candelilla, refined	67–79	152.6–174	63–68
Long leaf foilages, Japanese	67–80	152.6–176	—
Paraffin 152/154 AMP	67.8	154	66.1

Wax	Melting Point (°C)	Melting Point (°F)	Solidifying Point (°C)
"Petrowax A" (micro.)	69	156	67.8
Montan, bleached	69.5–84	157.1–185	—
Hydrogenated jojoba oil	70	158	—
Cork	70.5	159	—
Ozocerite, natural unbleached	70–79	158–174	—
"Utahwax," refined American ozocerite	70.7	159.3	—
Microcrystalline, amber 160/165 ASTM	71–74	160–165	—
Esparto	72.5–78	162.5–172.4	—
Douglasfir, commercial	72.8	163	
Orange peel	73–75	163.4–167	—
Coccid insect, Japanese	73–78	163.4–172.4	—
Montan, crude	73–82	163.4–179.6	—
Rod paraffin	74–76.7	165–170	—
Stearone, commercial	74–76.5	165–169.7	—
Sisal hemp	74–81	165–178	—
Ricebran	75–83	167–181.4	—
Shellac	75–84	167–183	—
"Superla," white (micro.)	75.3	167.5	—
Candelilla, high-melting species	76–77.4	169–171.3	63.8–67.7
Sorghum	77–82	170.6–179.6	—
"Be Square White" (micro.)	77.8–79.4	172–175	76.7
Microcrystalline, amber 170/175	77.8–79.4	172–175	—
Montan, crude	78–85	172.4–185	—
Ouricury, double-refined	79	174	68.9
Bamboo leaf	79–80	174–176	—
Sugarcane, refined	79–81	174–178	70.9
Pisang	79–81.5	174–178.7	—
Caranday	79.7–84.5	175.5–184	—
Apple skin	80	176	—
Stearone	80	176	—
Indian corn	80–81	176–178	—
Stearanilid	80–82	176–179.6	—
Fiber, refined	81	177.8	72.1
Sawpalmetto	81.3	178.3	—
Chinese insect	81.5–83	178.7–181.4	80–82
Raffia	82–83	179.6–180.4	—
Montan, American dark brown	82.2–87.7	180–190	—
Carnauba	83–86	181.4–186.8	80–84
"Halowax 1051 X" (69.5% Cl)	83.3–87.7	182–190	—
Ouricury, crude	83–87	181.4–188.6	72.2
Ocotillo	84	183	—
"Rilan Wax"	84–85	183.2–185	—

Wax	Melting Point (°C)	Melting Point (°F)	Solidifying Point (°C)
"Armid C" (C_{12} & C_{14} amides)	—	—	85
Palm, commercial	85–86	185–186.8	75
Silicon waxes	85–110	185–230	—
"Castorwax"	86	186.8	74.2
"Pale Yellow 180" (micro.)	87.4	189.3	85.5
Rhimba bark	88	190.4	—
Surakhansk ceresin	89	192	87.7
"Armid C"	90	194	85.0
Chlorowax (70% Cl)	90	194	—
"Nibren Wax D 88" (49% Cl)	92–96	197.6–204.8	—
"Norcowax C"	92.8	199	87.7
Palm, Colombian crude	93	199.4	—
Montanone	97	206.6	—
Polyethylene	97–106	206.6–223	—
"Armid HT"	—	—	98
"FT 200" (Fischer-Tropsch)	100–105.5	212–222	—
"Gersthofen Wax O" and "OP"	102–106	215.6–222.8	—
"Estawax"	103.7	218	—
"Armid 18" (stearamide)	104	219	—
Stearamide, pure	109	228.2	—
"FT Wax 300" (Fischer-Tropsch)	110	230	—
"Halowax 1052 X"	111–118	232–245.4	—
"Abril Wax 8NS"	119–122	246–251.6	116–120
"Seekay Wax," highest m.p.	120–125	248–257	—
"Nibren Wax D 130" (59% Cl)	130–134	266–273	—
"Armowax"	132–135	270–275	—
Cetyl acetamide	137–139	278.6–282	—
"Abril Wax 10DS"	138–142	280.4–287.6	140
"Acrawax C"	140–142	284–287.6	—
Cranberry, containing ursolic acid (m. 283°C)	217.5	423.5	—

Flash Points of Waxes

Flash, c.o.c., °F (ASTM D92-52)

"Aristowax"	
143/150	460
149/151	460
160/165	515
Beeswax, yellow	468–482
Beeswax, bleached	473–496
"Acrowax C"	545
"Amid HT"	437
"Armid C" (amide of coco fatty acids), m. 85°C	345
"Armowax" (methylene bis-stearamide), m. 250°C	482
Carnauba	
#2 yellow	520–620
North Country	520–600

	Flash, c.o.c., °F (ASTM D92-52)
"Estawax" (Lovell Chemical Co.)	605
"Esterol" (high mol. wt. alcohol)	499
Fischer-Tropsch	
"FT 200," m. 212°F	424
"FT 300," m. 221°F	536
Chlorinated paraffin	
125/127 grade chlorinated (11% Cl)	419
125/127 grade chlorinated (22% Cl)	464
"Fibrene Wax" (micro.), m. 128–133°F	460–470
Microcrystalline	
"Synceru," m. 157.5°F	425
"Petrosene"	470–490
"Petrowax A," m. 167.5°F	530
Amber 175/180°F	560
Amber 190/195°F	565
Paraffin	
128/130°F AMP	420
134/136°F AMP	420
143/145°F AMP	440–450
152/154°F AMP	470
Stearanilide	480
Stearone	510
"Polyethylene Glycol 1500"	430
"Polyethylene Glycol 4000"	535

Blocking Temperature and Tensile Strength of Various Paraffin Waxes and of Paraffins with Wax Polymers Added

Designation of Sample	Melting Point (°F) (ASTM D 87-42)	Blocking Temp. (°F) (Gradient Method)	Tensile Strength (lb/sq in)
CO – H	125.5	90/95	211
+ 1% ACP 6[a]	—	—	297
B[e]	128	92/95	186
H – 38[b]	130	97/108	175
H – 42	132	101/104[d]	185
A – 173[c]	134	95/100	200
+ 1% ACP 6	—	—	297
+ 5% ACP 6	—	103/103	413
H – 60	135	110/113[d]	200
C[e]	136.6	101/105	278
A – 191	139	105/110	230
+ 1% ACP 6	—	—	339
H – 87	140	115/120[d]	260, 275
M[e]	143.8	105/110[f]	308

[a] "ACP 6" refers to the polyethylene wax of the Semet-Solvay Petrochemical Division; [b] H numbers 38, 42, 60, and 87 correspond to durometer hardness values at 77°F; [c] A 173 is listed by the refiner as having a hardness of 50 at 95°F, and a modulus of rupture of 500 psi at 73°F; [d] blocking temperatures taken in a laboratory maintained at 73°F and 50% R.H.; [e] blocking and tensile measurements determined by W. R. Turner *et al.* [*Ind. Eng. Chem.*, **47**, 1223 (1955)]; [f] blocking temperature by mercury method (numerator shows "start to block" and denominator "blocking temperature."

Designation of Sample	Melting Point (°F) (ASTM D87-42)	Blocking Temp. (°F) Gradient Method)	Tensile Strength (lb/sq in)
CO – J	143–145	101/101	—
+ 1% ACP 6	—	—	368
+ 5% ACP 6	—	109/109	420
SW – 4415	145	115/115	—
SW – B	147	—	263 (70°)
SW – D	149	—	169 (70°)
O*	151.4	125/130	192
SW – 5512	154	138/138	151 (70°)
SW – C	164	—	235 (70°)

Variations of Tensile Strength with Variations in Temperature for Paraffin Wax (133°F AMP)

Temperature (°F)	Tensile Strength (psi)
77	200
70	240
65	250
50	260
34	140

* From Data Sheet C-46 American Resinous Chemical Corp.

Modulus of Rupture in Relation to Other Physical Constants of Paraffin Waxes

Designation of Sample	Melting Point (°F)	Viscosity SSU @ 210°F	Penetration @ 77°F	Blocking Temp. (°F)	Modulus of Rupture (psi)
SH-100	125.2	36.9	13	100	450
SH-120	131.8	38.4	15	100	520
SH-130	132.1	40.3	10	100	550
SH-173	134.0	40	16	95–100	500 (73°)
SH-200	139.8	41	9	110	500
SH-230	141.2	42	8	110	420
SH-270	141.5	43	8	115	600
SH-300	158.8	49	10	130	320
Dairy Wax P-PIB	—	—	—	—	700

Note: The figures given for modulus of rupture and other physical constants on samples designated here as SH-100, SH-120, etc. are those of the Shell Oil Company. Dairy Wax P-PIB is a milk carton wax of the composition: 98 paraffine 126/128, 2 parts polyisobutyl polymer. It had a tensile strength of 420 psi.

Composition of Paraffin Waxes—Percentage by Weight*

Melting Points (°F)	n-Paraffins	Isoparaffins	Cycloparaffins[b]	Alkyl Benzenes
125.5–127.6	59.9–81.4	5.5–13.4	8.5–21.6	0.4–0.9
128.0–130.6	86.1–92.3	3.5–6.3	3.0–7.1	0.2–0.5
135.4–137.3	81.1–84.2	5.9–7.1	9.4–12.8	0.2
141.6–144.0	89.2–91.7	5.5–13.0	2.8–8.5	—
151.4	84.4	13.4	2.2	—

* Percentage composition obtained by mass spectrometer analyses of Turner, Brown, and Harrison (1955); cycloparaffinic materials composed of C_5 and C_6 rings.

Number of Carbon Atoms in the N-Paraffins of Paraffin Waxes

Melting Points (°F)	Range	Predominating
125.5–127.6	16–34	21–27
128.0–130.6	17–35	23–28
135.4–137.3	18–36	25–30
141.6–144.0	19–37	26–31
151.4	20–38	28–33

Note: The numbers of carbon atoms in the isoparaffins, cycloparaffins, and alkyl benzenes are of a somewhat higher range than those given for the normal paraffins.

Mean Values of Refractive Indices of Various Waxes at t°C

	$n_D^{t_1}$	$n_D^{t_2}$	$n_D^{t_3}$	$n_D^{t_4}$
Bayberry	1.4504 @ 45	1.4450	1.4360	—
Beeswax	1.4557	1.4480	1.4408	1.4329
Candelilla	—	1.4625	1.4585 @ 85	1.4519
Carnauba	1.4696	1.4630	1.4540	1.4468
Cetyl palmitate	—	1.4429	1.4398 @ 70	—
Chinest insect	1.4566	1.4490	—	—
Chinese tallowtree	1.4827 @ 25	—	—	—
Jasmine flower	—	1.4622	—	—
Jojoba (liquid)	1.4648 @ 25	—	—	—
Kapok lint	1.4618	—	—	—
Microcrystalline				
160/165	—	1.4427	1.4345	—
170/175	—	1.4446	1.4369	
180/185	—	1.4466	1.4394	—
Montan	—	—	—	1.4670
Ouricury	—	—	—	1.4478
Palmitic acid	—	1.4346	1.4272	—
Paraffin, American				
M.P. 121°F	1.5040	1.4349	1.4239	—
M.P. 126°F	1.5071	1.4352	1.4262	—
M.P. 128°F	1.5084	1.4353	1.4267	—
M.P. 131°F	1.5103	1.4358	1.4272	—
M.P. 136°F	1.5163	1.4370	1.4285	—
M.P. 141°F	1.5241	1.4383	1.4306	1.4200
Paraffin, Asiatic				
M.P. 146°F	—	1.4396	1.4311	—
Ricebran	1.4686 @ 30	—		—
Rod, petroleum (m. 177°F)	—	—	1.4377 @ 84	—
Soybean	—	1.4419 @ 65	—	—
Spermaceti	—	1.4400	1.4397 @ 70	1.4255
Stearic acid	—	1.4337 @ 70	1.4299	—
Stearone	1.5164	—	—	—
Sugarcane	1.5100 @ 25	—	—	—
Ucuhuba	1.4614	—	1.4446 @ 70	—
Woolwax (anhydrous lanolin)	1.4801	1.4650	—	—

Mean Values of Specific Gravities of Waxes

Wax	Solid @15°C	Solid @25°C	Melt @100°C
"Armid C"	—	0.890	—
Bamboo leaf	0.964	0.961	0.819 (98°C)
Bayberry	0.989	0.980	0.876 (98°C)
Beeswax, yellow commercial	0.949	0.943	0.822
Beeswax, yellow USP	0.968	0.958	0.846 (98°C)
Beeswax, white USP	0.967	0.955	0.848
Candelilla (m. 70.5°C)			
in lumps as received	0.996	0.992	0.855
melted and recast	0.984	0.980 (26°C)	0.855
Cape berry, S. African	0.995	0.988	0.874
Caranday	0.997	0.990	—
Carnauba	0.999	0.997	0.842 (98°C)
"Castor Wax"	0.996 (20°C)	0.989	0.896
Ceresin, imported	0.927	0.920	0.777 (98°C)
Cetyl alcohol	—	0.815 (55°C)	0.784
Chinese insect	0.951	0.946	0.810 (99°C)
Chinese tallowtree	0.941	—	—
Chlorinated hard paraffin			
11% Cl	0.860	—	decomposes
22% Cl	0.958	—	decomposes
33% Cl	1.072	—	decomposes
44% Cl	1.204	—	decomposes
70% Cl ("Chlorowax")	—	1.640	decomposes
Cotton	—	0.998	0.886 (95°C)
Cranberry	0.975	0.970	—
Douglasfir bark	1.050 (20°C)	—	—
Esparto	0.988	0.987	0.837 (98°C)
Fiber	0.978	0.956	—
Flax	0.974	—	0.830 (98°C)
Fischer-Tropsch			
"FT Wax 200"	0.925 (20°C)	—	0.750 (130°C)
"FT Wax 300"	0.933 (20°C)	—	0.752 (120°C)
"Gersthofen Wax CR"	1.006 (20°C)	—	—
"Gersthofen Wax CP"	1.050	1.040	0.863 (118°C)
Ghedda (Batatavia)	0.958	0.950	—
"I. G. Wax Z"	0.942	0.936	0.779 (112°C)
Japanwax	0.994	0.978	0.873
Jasmine flower	0.960	—	0.826
Jojoba (liquid)	—	0.864	—
Lignite paraffin (m. 58°C)	0.920	0.915 (20°C)	—
Microcrystalline			
150/155°F ASTM	0.913	—	0.768
160/165°F ASTM	0.928	0.921	0.763
170/175°F ASTM	0.935	0.929	0.761
180/185°F ASTM	0.939	0-934	0.770
190/200°F ASTM	0.943	—	0.790
Montan, American	1.030 (20°C)	—	—

Wax	Solid @ 15°C	Solid @ 25°C	Melt @ 100°C
Montan, European	1.010	—	—
Mimosa floral	0.957	—	—
Ouricury, crude	0.995	0.989	0.859 (98°C)
Ouricury, refined (m. 83°C)	1.056	1.053	0.865
Ozocerite, European crude	0.952	—	—
refined (m. 75°C)	0.907	0.903	0.796
American ("Utahwax")	0.935	0.929	0.885 (60°C)
Palm, Colombian	1.020	1.016	0.859 (98°C)
Paraffin, American			
M.P. 121°F	0.896	0.880	0.752
M.P. 126°F	0.909	0.899	0.753
M.P. 128°F	0.910	0.901	0.754
M.P. 131°F	0.911	0.902	0.754
M.P. 136°F	0.917	0.909	0.756
M.P. 145°F	0.925	0.916	0.759
M.P. 154°F	0.928	0.920	0.765
Paraffin, Asiatic			
M.P. 146°F	0.915	—	0.773 (85°C)
Polyethylene	—	0.925	—
"Polyethylene Glycol 1500"	1.151 (20°C)	—	—
"Polyethylene Glycol 4000"	1.204 (20°C)		
Raffia	0.950	—	0.834 (99°C)
Ricebran	—	0.915 (30°C)	—
Scale wax, crude	0.873	0.863	0.761
Sisal hemp	1.009	—	—
Spermaceti	0.952	0.941	0.812
Stearamide	0.800	—	—
Stearic acid USP	0.958	0.952	0.835 (90°C)
Stearone	—	0.983	—
Sugarcane	0.997	0.992	0.837
Ucuhuba	0.995	—	0.884 (50°C)
Woolwax (anhydrous lanolin)	—	0.942	—

Coefficient of Density Change Per One Degree Centigrade

Kind of Wax	Temperature Range (°C)	Density Change	Density Coefficient
Candelilla, raw	28.8–44.4	0.9911–0.9823	0.00053
m. 71.0°C	20–30 (computed)	0.9953–0.9900	0.00053
	77–100 (melt)	0.8670–0.8550	0.00052
Same wax, remelted	26.1–39.7	0.9803–0.9752	0.00039
	39.7–47.2	0.9752–0.9703	0.00065
	20–30 (computed)	0.9840–0.9800	0.00040
Carnauba, raw	25–38	1.0010–0.9980	0.00023
m. 84.2°C	38–44	0.9980–0.9970	0.00017
	20–30 (computed)	1.0020–0.9990	0.00030
	90–100 (melt)	0.8484–0.8415	0.00069
Same wax, remelted	24.4–38.0	0.9990–0.9950	0.00029
	38–44	0.9950–0.9930	0.00033
	20–30 (computed)	0.9830–0.9995	0.00035

Kind of Wax	Temperature Range (°C)	Density Change	Density Coefficient
Ouricury, crude	22–27	1.0668–1.0655	0.00026
m. 84.3°C	27–35	1.0655–1.0626	0.00035
	27–37	1.0655–1.0616	0.00039
	95–100 (melt)	0.9010–0.89990	0.00040
Ouricury, refined	24–30	1.0539–1.0516	0.00038
m. 79.0°C	90–100 (melt)	0.8700–0.8650	0.00050
"I.G. Wax Z"	25–35	0.9360–0.9300	0.00060
m. 102°C	112–122 (melt)	0.7790–0.7740	0.00050
"Gersthofen Wax OP"	25–35	1.0400–1.0298	0.00102
m. 107°C	118–127 (melt)	0.8630–0.8570	0.00067
Bayberry, raw	10–23	1.0028–0.9916	0.00086
Bayberry, remelted	10–23	1.0293–1.0211	0.00063
Beeswax, yellow	15–25	0.9677–0.9580	0.00097
m. 64.0°C	20–30 (computed)	0.9625–0.9510	0.00117
	74–96 (melt)	0.8650–0.8490	0.00072
Beeswax, white	10–15	0.9698–0.9664	0.00068
m. 65.0°C	15–25	0.9664–0.9547	0.00117
	71–96 (melt)	0.8671–0.8505	0.00066
"Castorwax," m. 80°C	24–35	0.9896–0.9857	0.00035
	90–100 (melt)	0.9030–0.8960	0.00070
Esparto	12–15	0.9891–0.9880	0.00037
	15–25	0.9940–0.9900	0.00060
Ghedda (Batavia)	10–15	0.9649–0.9603	0.00092
	15–23	0.9603–0.9524	0.00099
Japanwax	10–15	0.9976–0.9944	0.00065
	15–25	0.9935–0.9780	0.00155
Ozocerite, "JAA"	24–35	0.9010–0.8921	0.00081
m. 75.0°C	85–98 (melt)	0.8070–0.7960	0.00085
Paraffin (AMP)			
118/120°F	10–15.6	0.902–0.895	0.00125
	15.6–25	0.895–0.878	0.00181
	20–30 (computed)	0.887–0.866	0.00210
	57–100 (melt)	0.780–0.760	0.00061
124/126°F	15–26.6	0.909–0.897	0.00106
	20–26.6	0.9046–0.897	0.00115
	20–30 (computed)	0.9046–0.892	0.00126
128/130°F	15–25	0.9086–0.8996	0.00090
	20–30 (computed)	0.9048–0.894	0.00108
	60–100 (melt)	0.780–0.759	0.00053
134/136°F	10–15.6	0.9175–0.914	0.00062
	15.6–25	0.914–0.907	0.00074
	20–30 (computed)	0.911–0.902	0.00090
	69–100 (melt)	0.772–0.753	0.00059
138–140°F	15.6–21	0.914–0.910	0.00075
	21–25	0.910–0.906	0.00100
	20–30 (computed)	0.9108–0.901	0.00098
	70–100 (melt)	0.778–0.763	0.00050
143/145°F	15.6–21	0.925–0.920	0.00090

Kind of Wax	Temperature Range (°C)	Density Change	Density Coefficient
	20–30	0.921–0.9125	0.00085
	72.8–100 (melt)	0.778–0.763	0.000555
152/154°F	15.6–21	0.9275–0.923	0.00082
	20–30	0.9240–0.9160	0.00080
	78–100 (melt)	0.7780–0.7640	0.00064
Spermaceti, m. 47°C	24.5–35	0.9371–0.9269	0.00091
	20–30 (computed)	0.940–0.9315	0.00085
	50–100 (melt)	0.837–0.812	0.00057

Coefficient of Volume Expansion of Waxes

Wax	Solid/25°C	Melt/100°C
Beeswax, yellow	0.00123	0.00092
Beeswax, white	0.00126	0.00087
Candelilla	0.00040	0.00061
Carnauba	0.00031	0.00082
"Castorwax"	0.000355	—
Ceresin, artificial m. 166°F	—	0.000585
"Gersthofen Wax OP"	0.000990	0.00078 (melt/110°C)
"I.G. Wax Z"	0.000645	0.00065 (melt/110°C)
Lauric acid	0.00087 (35°C)	0.00092
Microcrystalline		
160/165°F ASTM	0.00104	0.00059
165/170°F ASTM	0.00070	0.00068
180/185°F ASTM	0.00029	0.00080
Myristic acid	—	0.00080
Ouricury, crude	0.00024	0.00060
Ouricury, refined	0.00036	0.00067
Ozocerite "JAA," m. 167°F	0.00091	0.00107
Palmitic acid	—	0.00085
Paraffin		
m. 121°F (47.2°C)	0.00206	
m. 126°F (52.2°C)	0.00128	
m. 131°F (55.0°C)	0.00094	
m. 136°F (57.5°C)	0.00089	
m. 141°F (60.5°C)	0.00082	
m. 128/130°F AMP	0.00121	0.00070
m. 134/136°F AMP	0.00100	0.00078
m. 138/140°F AMP	0.00109	0.000655
m. 143/145°F AMP	0.00093	0.00072
m. 152/154°F AMP	0.00087	0.00070
Spermaceti	0.00097	0.00070
Stearic acid	0.00058 (20°C)	0.00084
Sugarcane	0.00050 (20°C)	—

Note: The coefficient of expansion is calculated for each wax from the formula $\beta = \frac{d_1 - d_2}{d_2 t}$ derived from the formula $\beta = \frac{v_2 - v_1}{v_1 t}$, where t is the difference in temperature at which the density determinations are taken, and v_1 and v_2 represent the volumes of 1 gram of wax at temperatures t_2 and t_1. The coefficient for the waxes in liquid condition is taken at a temperature just above the melting point and 100°C except where otherwise indicated.

Volume Decrease of Waxes During Solidification and Crystallization Computed by Graef's Formula:

$$C = 100 - 100 \frac{\text{density liquid}}{\text{density solid}}$$

For computation the density of the melt is taken at 10 degrees C above melting point; the density of solid is taken at 25°C.

	(%)
Waxes from Insects:	
Apis—	
Beeswax, yellow	9.78, 9.60
Ghedda	9.45
Coccid—	
Chinese insect	15.18
Lac	14.55
Waxes from Mammals:	
Land—Woolwax	8.00
Marine—Spermaceti	10.58
Waxes from Plants:	
Palm tree group—	
Bamboo leaf	14.15
Carnauba	15.35
Ouricury	17.47
Palm, Colombian	13.40
Shrubs and canes—	
Candelilla	11.92
Sugarcane, m. 80°C	16.58
Fibers and grasses—	
Esparto	14.88
Flax	13.76
Raffia	11.70
Waxes from Barks:	
Douglas fir	13.0
Waxes from Berries:	
Bayberry	9.10
Japanwax	10.16
Hydrocarbons:	
Microcrystalline	
Amber amorphous 150/155°F ASTM	12.84
"Be Square White" 163/165°F ASTM	12.86
Tank Bottom 165/170°F ASTM	13.68
Pale Yellow, Oklahoma 185/190°F ASTM	15.68
Macrocrystalline	
Paraffin 118/120 AMP	11.16
124/126 AMP	12.34
128/130 AMP	13.30
134/146 AMP	14.32
138/140 AMP	14.08
152/154 AMP	14.85

	(%)
Synthetic wax:	
"Castorwax"	8.72
Higher Fatty Acids:	
Stearic acid	12.16

Dielectrical Properties of Waxes

Wax	Dielectric Constant (K) (at 1000 cycles) Temp. 24–25°C	Volume Resistivity (VR) (10^{13} ohms cm) Temp. 24–25°C
Bayberry	3.22–3.27[a]	2–5[a]
Béeswax	2.87	5–12[a]
Candelilla, m. 65°C	2.38–2.49[a]	>290[a]
Candelilla, m. 66–73°C	2.50–2.63	120
Carnauba, m. 78°C	2.66–2.83[a]	60–120[a]
Ceresin, m. 70–73°C	2.16–2.24[a]	>290[a]
Cetyl alcohol	2.94	—
Chinese insect, m. 65°C	2.94–2.98[a]	1–2[a]
Cotton	3.00	6.8 (1×10^{12} ohms cm)
"Crown 500," (micro.), m. 184°F	2.79 (20°C)	640 (22°C)
"Crown 1035" (micro.), m. 190°F	2.45 (20°C)	380 (22°C)
Fischer-Tropsch, "FT Waxes 200 & 300"	3.00	1000
"Estawax"	1.90 (1×10^6c)	—
"Halowax 1051 V"	3.70	—
"Halowax 1052 X"	3.63–3.83[a]	4–9[a]
Japanwax, m. 50°C	2.96–2.99[a]	6–7[a]
"Micris 777 Yellow" (micro.)	2.06	3.66 (100c)
"Micro," m. 63.3°C	2.20	>60
Montan, m. 80–82°C	2.62–2.67[a]	>290[a]
Opalwax (120-hydroxystearin)	12 (30°C, 100c)	—
Ozocerite		
Crude imported	2.37–2.43[a]	30–40[a]
Refined	2.03	3.6
Domestic	2.63	—
Palmitic acid	2.34 (70°C)	—
Paraffin, m. 51.7°C	2.21–2.34[a], 2.27	>290,[a] 1000[b]
Polyethylene (wax)	2.24–2.25 (1×10^6c)[c]	140–150[c]
"Santowax R"	2.58	14(100°C), 3.5(135°C)
"Seekay Wax"	5.40	—
Spermaceti	3.60–3.75[a]	3–4[a]
Stearic acid, m. 55.5°C	2.37–2.41[a]	3–7[a]
"Superla" (micro.), m. 74°C	2.32–2.35[a]	>460
Synthetic wax "PS/43," m. 63.5°C	2.20	—
Zinc stearate	2.58[a]	640[a]

Wax	Effective A-C Conductivity (10^{-18} mho cm)	Dielectric Strength (BV) (volts per mil) Temp. 25°C	Dielectric Power Factor (PF) (1000 c.p.s.) Temp. 25°C
"Acrawax C"	—	428	0.0277
Bayberry, m. 60°C	89–105[a]	—	—
Beeswax	45–48[a]	—	—
Candelilla, m. 65°C	6–6.4[a]	—	—
Candelilla, m. 66–73°C	19	—	—
Carnauba, m. 78°C	4.9–5.3[a]	—	—
Ceresin, m. 70–73°C	<0.37[a]	—	—
Chinese insect, m. 65°C	125–137[a]	—	—
Cotton	—	—	0.032
"Crown 500" (micro.), m. 184°F	—	1500 (20°C) 780 (40°C)	0.0003 (20°C)
"Crown 1035," m. 190°F	—	2050 (20°C), 710 (40°C)	0.0150 (20°C)
"Estawax"	—	770	0.012 (10^4 cps)
Fischer-Tropsch "FT 300 & 500"	—	550–630	—
"Halowax 1052 X"	4.4–7.4[a]	—	0.0011
Japanwax, m. 50°C	9–12[a]	—	—
"Micris 777 Yellow" (micro.)	—	—	0.0011
"Micro Wax," m. 63.3°C	—	510	0.0002
Montan, m. 80–82°C	29–31[a]	—	
"Nibren" (K 4.5–5.5)	—	—	0.0004–0.0030
Ozocerite, crude imported	10–12[a]	—	—
Ozocerite, refined	—	1180	0.0300
Paraffin, m. 51.7°C	<0.37[a]	787–984[b]	—
Paraffin, single crystals	—	5500	—
Petrolatum	—	230–300	—
Polyethylene (wax)	—	580–720	0.0003[d]
Shellac wax	—	356–416	—
Spermaceti	6–6.6[a]	—	—
Sperm oil	—	230–497	—
Stearic acid, m. 55.5°C	4.4–4.6[a]	—	—
Sugarcane	—	882	—
"Superla" (micro.), m. 74°C	4.2–4.6[a]	—	—
Synthetic, "PS/43," m. 55.6°C	—	474	0.002 (1×10^6 cps)

[a] Lee, J. A., and Lowry, H. H., *Ind. Eng. Chem.*, **19**, 302–306 (1927). The dielectric constant, effective A-C conductivity, and the volume resistivity were obtained by calculation from the capacitance, conductance, and insulation resistance values. [b] Austin, A. E. V., and Pelza, N., *J. Inst. Elect. Engrs. (London)*, **93**, Pt. 1, 526–532 (1946). [c] Value for polyethylene of about 2000 mol. wt. Resin of 21,000 mol. wt. has a dielectric strength of 1000–1100. [d] Dissipation factor.

Solubility of Waxes in Various Solvents (Expressed in grams per 100 grams solvent at 25°C unless otherwise stated)

Wax	Ethanol (95%)	Benzene	Toluene	Xylene
Beeswax	0.41,[e] 0.43	23.0, 24.8[b]	18.2 (22°C)[a]	9.48[a]
Candelilla	0.49	2.44 (18°C)[a]	9.8[a]	7.55[a]
Carnauba	0.17[e]	1.38 (18°C)[a]	3.1[a]	0.72[a]
	0.15 (18°C)[a]	—	2.6 (22°C)[a]	—
Cotton	3.7	15.0[g]	12.0[g]	13.0[g]
Esparto	0.30[b]	7.56 (22.5°C)	13.0 (22.5°C)[a]	—
Japanwax	1.76[b]	49.3 (22.5°C)[a]	59.8 (23.3°C)[a]	—
Laurone, m. 67°C	0.5	10.5[h]	—	—
Microcrystalline				
170/175	0.01	18.0[a]	14.6[a]	16.0
180/185	nil	5.27[a]	7.6[a]	—
Ouricury	0.08,[a] 0.21[b]	0.94 (18°C)[a]	3.3[a]	—
Ozocerite	0.22[b]	1.99[d]	3.83[d]	3.98[d]
Palmitone, m. 76.5°C	nil	0.7[b]		—
Paraffin				
125/127	0.12[e]	27.5	31.0[f]	—
	0.044 (22°C)[e]	11.8 (20°C)	11.0 (20°C)[f]	—
131/133	0.014	20.7	25.8 (23.3°C)[f]	—
		8.32 (18°C)[a]	9.74 (19°C)[f]	9.90 (19°C)[e]
Shellac	0.08[b]	3.19 (24°C)[a]	9.8 (23.3°C)	4.85[a]
Spermaceti	0.74[b]	65.0 (22.5°C)[a]	—	—
Stearone, m. 76°C	nil	0.4[h]	—	—
Sugarcane	1.51, 1.81[b]	11.5 (22.5°C)[a]	8.67 (23°C)	6.70[a]

Wax	Turpentine	Naphtha[a]	Solvenol	Acetone
Beeswax	8.0 (24°C)	3.5[g], 5.0[b]	6.0	—
	44.0 (40°C)	37.0 (40°C)	36.0 (40°C)	
Candelilla	3.6,[b] 4.8	3.6[g], 4.0[b]	4.0	
	33.0 (40°C)	—	35.0 (40°C)	
Carnauba	0.8, 1.7[e]	0.3,[g] 0.4[b]	1.6	0.40[e]
	4.9 (40°C)[d]	2.0 (40°C)	4.0 (40°C)	
	11.0 (45°C)[d]	3.0 (45°C)	7.0 (45°C)[i]	
Cotton	17.0[j]	—	—	4.7[j]
Montan (refined)	3.0 (27.5°C)[b]	2.4[b]	6.0[b]	—
	24.0 (40°C)	6.0 (40°C)	27.0 (40°C)	—
Ozocerite	6.1	4.6,[g] 11.5[e, f]	—	0.27[e]
Paraffin				
125/127	29.2 (26.7°C)[d]	30.0 (20°C)[f]	—	0.75[b], 9.2 (50°C)
133/135	19.2 (26.7°C)[d]	12.0, 18.0 (24°C)[f]	—	0.50

[a] V.M. & P. naphtha unless otherwise stated; [b] solubility by Pickett, O. A., Hercules Powder Co., cf. *Ind. Eng. Chem.*, **21**, 767 (1929); [c] solubility by Warth and Bulatkin (1947); [d] listed by "Commercial Waxes" by Bennett (1944); [e] solubility by Pawlewski (1889); [f] petroleum ether as solvent; [g] varnoline as solvent; [h] solubility by Poole, J. W., *Ind. & Eng. Chem.*, **21**, 1101 (1929); [i] solubility as listed in "Chemistry and Technology of Waxes," 1st Ed. (1947); [j] solubility by Tonn and Schoch, *Ind. & Eng. Chem.*, **38**, 415 (1946).

Solubility of Waxes in Various Solvents

(Expressed in grams per 100 grams solvent at 37°C (98.6°F) unless otherwise stated)

Wax	Ethanol (95%)	Benzene	Ethylene Dichloride
Bayberry	1.12 (25°C)[b]	—	24.1[b]
Beeswax	0.95 (35°C)[b]	41.0 (35°C)[b]	2.76
Candelilla	3.12	4.0	—
Carnauba	0.25	2.7	—
Cotton	5.3[e]	28.0[e]	—
Esparto	2.04[a]	14.0	1.18[b]
Japanwax	7.16[a]	v. high	43.5[d]
Microcrystalline			
170/178	0.11[a]	30.0	2.0
180/185	0.07[a]	9.0	—
Ouricury	0.50	1.8	0.38[b]
Paraffin 125/127	0.36[a]	42.0 (30°C)[f]	24.2 (38°C)
Shellac	0.40[a]	6.0	0.95[b]
Spermaceti	2.40[a]	v. high	40.0[b]
Sugarcane	0.75	15–20	1.28[b]

[a] Solubility by McBeth (1954); [b] solubility by Warth and Bulatkin (1946); [d] listed in "Chemistry and Technology of Waxes," 1st Ed. (1947); [e] solubility by Tonn and Schoch, *Ind. Eng. Chem.*, **38**, 415 (1946); [f] solubility by Moos and Haas (1948), cf. *Chem. Abstracts* **44**, 4236 (1950); solubility in toluene 58 at 35°C.

Saponification Numbers of Lipide Waxes

	Reported Values	Mean Value
Group I[a]:		
Norway spruce	254	254
Cay-cay (Cochin-China wax)	235–248	241.5
Murumuru	238–242	240
Conifer needle waxes	215–241	228
Japanwax	206–237	221.5
Myrtle, Jalapa (m. 43.2°C)	214.5	214.5
Bayberry	208–217	212.5
Chinese tallowtree	204–222	213
Myristica waxes	180–239	209.5
Karagami (a japanwax)	199.4	199.4
Ocotillo bark	182–188	184
Cranberry skin[b]	181	181
Coccin insect waxes	125–213	169
Douglasfir	138–190	164
Group II:		
Tsingtao insect	146–150	148
Madagascar waxes	140–150	145
Doegling oil	123–144	133.5
Sugarcane wax, crude	98–168	133
Sperm oils	123–133	128
Spermaceti	120–135	127.5
Mutton bird oil	120–126	123

	Reported Values	Mean Value
Hemp	86–160	123
Spanish moss	120–121	120.5
Ceroplastes insect waxes	97.5–139	118.3
Trigona (bee)	80–146	113
Silk coccoon	105–115	110
Maté leaf	110	110
Cotton	109	109
Pisang leaf	106–109	107.5
Candelilla, crude (m. 77.4°C)	104–108	106
Orange peel	90–121	105.5
Woolwax, ordinary commercial	82–127	104.5
Ghedda (East Indian beeswax)	85–119	102
Woolwax (anhydrous lanolin, USP)	90–106	98
Beeswax, yellow, USP	86–97	91.5
Ouricury	67–115	91
Colombian palm	74–105	89.5
Retamo	85–89	87.5
Chinese insect	80–93	86.5
Flax	70–100	85
Carnauba	78–89	83.5
Indian lac	79–83	81
Ricebran	57–104	80.5
Group III:		
Caranda	66–80	73
Esparto	67–78	72.5
Sugarcane, refined	65–77	71
Fiber	61–79	70
Floral waxes	31–105	68
Sisal hemp	56–58	57
Candelilla, resinous	47–65	56
Oleander bark	50–56	53
Raffia	50–54	52
Candelilla, refined	46–56	51
Bamboo leaf	41–46	43.5
Cauassu leaf	29–40	34.5
Sorghum waxes	16–44	30

[a] Group I. Waxes with mean saponification numbers upward of 150. Most of these waxes are vegetable tallows.

Group II. Waxes with mean saponification numbers between 80 and 150. Includes all of the insect, land- and animal waxes, as well as a number of vegetable waxes. Includes montan wax, a mineral wax.

Group III. Waxes with mean saponification numbers between 30 and 80. Includes most of the plant waxes.

[b] Cold-extracted with hexane. The wax extracted by hot solvents has a much lower saponification number.

Saponification Numbers for Waxes by Hezel Method

Wax	International Commission	Hezel Method
Beeswax, bleached	84.2–85.3	91.1–93.3[a]
Beeswax, pure yellow	79.7–80.6	91.0–91.7[a]
Beeswax, crude	34.4–35.9	37.1–37.6
Beeswax-paraffin 50:50	30.3	34.7–34.9
Carnauba wax	71.7–75.8	81.3–81.9[a]
Candelilla wax	54.8–55.4	59.4–60.3[a]
Montan wax, crude	74.4–75.5	79.7–81.2[a]
Montanilla wax white, extra	18.4–18.7	23.3–23.6
Montan cable wax AA	13.8–14.2	15.0–15.1
"I. G. Wax L"	150.8–151.9	150.8–152.4
"I. G. Wax OP"	117.8–119.9	187.4*
"I. G. Wax Spezial"	105.2–107.2	109.1–110.6

Note: The Hezel method consists in heating to 130°C for 2 hr 3–5 g of wax with 40–50 ml of approx. 0.5*N* KOH solution in ethylene glycol in a covered 250-ml Florence flask placed inside an oven; a little xylene can be added to make the mixture fully soluble. * Discrepancy traced to the presence of Ca soap (0.72 per cent Ca). [a] Values are no higher than the optimum obtained by other methods employing suitable organic solvents.

Two-Way Temperature Conversion Table

(°C)		(°F)	(°C)		(°F)	(°C)		(°F)
−40.0	−40	−40	2.78	37	98.6	21.7	71	159.8
−34.4	−30	−22	3.33	38	100.4	22.2	72	161.6
−28.9	−20	− 4				22.8	73	163.4
−23.3	−10	14				23.3	74	165.2
−17.8	0	32				23.9	75	167.0
−17.2	1	33.8				24.4	76	168.8
−16.7	2	35.6				25.0	77	170.6
−16.1	3	37.4				25.6	78	172.4
−15.6	4	39.2				26.1	79	174.2
−15.0	5	41.0	3.89	39	102.2	26.7	80	176.0
−14.4	6	42.8	4.44	40	104.0	27.2	81	177.8
−13.9	7	44.6	5.00	41	105.8	27.8	82	179.6
−13.3	8	46.4	5.56	42	107.6	28.3	83	181.4
−12.8	9	48.2	6.11	43	109.4	28.9	84	183.2
−12.2	10	50.0	6.67	44	111.2	29.4	85	185.0
−11.7	11	51.8	7.22	45	113.0	30.0	86	186.8
−11.1	12	53.6	7.78	46	114.8	30.6	87	188.6
−10.6	13	55.4	8.33	47	116.6	31.1	88	190.4
−10.0	14	57.2	8.89	48	118.4	31.7	89	192.2
− 9.44	15	59.0	9.44	49	120.2	32.2	90	194.0
− 8.89	16	60.8	10.0	50	122.0	32.8	91	195.8
− 8.33	17	62.6	10.6	51	123.8	33.3	92	197.6
− 7.78	18	64.4	11.1	52	125.6	33.9	93	199.4
− 7.22	19	66.2	11.7	53	127.4	34.4	94	201.2
− 6.67	20	68.0	12.2	54	129.2	35.0	95	203.0
− 6.11	21	69.8	12.8	55	131.0	35.6	96	204.8

(°C)		(°F)	(°C)		(°F)	(°C)		(°F)
− 5.56	**22**	71.6	13.3	**56**	132.8	36.1	**97**	206.6
− 5.00	**23**	73.4	13.9	**57**	134.6	36.7	**98**	208.4
− 4.44	**24**	75.2	14.4	**58**	136.4	37.2	**99**	210.2
− 3.89	**25**	77.0	15.0	**59**	138.2	37.8	**100**	212.0
− 3.33	**26**	78.8	15.6	**60**	140.0	43	**110**	230
− 2.78	**27**	80.6	16.1	**61**	141.8	49	**120**	249
− 2.22	**28**	82.4	16.7	**62**	143.6	54	**130**	266
− 1.67	**29**	84.2	17.2	**63**	145.4	60	**140**	284
− 1.11	**30**	86.0	17.8	**64**	147.2	66	**150**	302
− 0.56	**31**	87.8	18.3	**65**	149.0	71	**160**	320
0	**32**	89.6	18.9	**66**	150.8	77	**170**	338
0.56	**33**	91.4	19.4	**67**	152.6	82	**180**	356
1.11	**34**	93.2	20.0	**68**	154.4	88	**190**	374
1.67	**35**	95.0	20.6	**69**	156.2	93	**200**	392
2.22	**36**	96.8	21.1	**70**	158.0	99	**210**	410
						100	**212**	413

Example 1. 42° Fahrenheit to be converted to Centigrade: Find 42 in the center column (*bold face type*) and read 5.56° C to the left.

Example 2. 42° Centigrade to be converted to Fahrenheit: Find 42 in the center column (*bold face type*) and read 107.6° F to the right.

Addenda

The Compounding of Waxes

When a small amount of one kind of wax of a much higher melting point (No. 1) is melted with a much larger amount of a relatively low melting point (No. 2), the resultant congealed wax product will melt at a temperature which will indicate a state of (a) solid solution with No. 1 the solute, and No. 2 the solvent, *i.e.*, a double phase system; (b) a simple wax mixture (single phase); (c) a true compound; or (d) an incompatible mixture.

In system (a), No. 1 greatly elevates the melting point of No. 2, as sugar elevates the boiling point of water. Under certain conditions No. 2 may liquate out, just as water will separate from a sugar solution.

In system (b) when the melting points are plotted against the percentage composition the curve is a straight line or nearly so; *e.g.*, mixtures of the paraffins; or waxes of similar molecular weight and type, such as the vegetable waxes.

In system (c) eutectic compounds with melting points lower than No. 1 are formed, and the plotted curves flex sharply downward; *e.g.*, melts made with pure palmitic and stearic acids.

In system (d) the No. 1 constituent tends to gravitate out even though it may be miscible in the melt. That very small portion which is soluble acts like (a), but a larger portion is simply dispersed.

There are also instances where more than one system is involved as can readily be seen by a study of the areas involved in the plotted curves.

Compounded or blended waxes when prepared on a commercial scale are made by melting the different waxes in a steam jacketed or electrical heated kettle made of aluminum or stainless steel. If electrically heated, the heating units are extended over the lower two-thirds of the vessel so as to avoid overheating at the top. The units must be properly packed with insulating material and wrapped on the outside so as to focus the heat on the interior of the kettle through the walls of the vessel. The lower melting point wax is melted first, and the higher melting waxes are then added. The blending of the waxes is effected by stirring them with a wooden paddle, although a double blade mechanical stirrer is to be preferred. In melting waxes it is best to carry out the process at a temperature of not over 28° (50°F) above the melting point of the finished wax compound, in order to avoid any alteration of the composition of the components. A melting kettle usually has a gate valve at the bottom or to one side of the vessel.

After opening the gate the melted wax should be strained through a fine metal screen, or through layers of cheese cloth, into an enamel-lined or other suitable pail with a broad pouring lip, from which the wax is poured into pans and permitted to solidify. These pans are either oblong or round and tapered. Pans made of aluminum are the most satisfactory. The wax is allowed to cool at room temperature until it becomes perfectly solid, but the removal of the wax is greatly facilitated by immersing the pan with the wax in ice water for a few minutes before tapping the bottom of the inverted pan to remove the cake of wax.

Author Index

(Page in boldface indicates that author's name appears in the reference list on that page.)

Abraham, E. P., 46
Abramowitz, W. L., 804, 865
Abrams, Allen, 515, 522, 641, 642, 803, 865
Adam, N. K., 20, 34, 66, 71
Adams, C. E., 43, 72
Adams, E. W. 409, 441, 792, 865
Adams, Roger, 43, 46, 72, 74, 76
Adati, S., 481, 496
Adickes, F., 46, 71
Adkins, H., 69, 75
African Sisal and Produce Co., Ltd., 209
Aguiar and Mello (Lisbon), 256
Ahmad, N., 330
Ahrens, 89
Aktiebolaget Lackljus, 841, 865
Albrecht, H., 48, 71
Alcocer, Gabriel, 189, 191, 330
Alcock, R. S., 732, 865
Alikonis, J. J., 735, 865
Allan, John, 203, 205, 207, 318, 319, 334, 337
Allan, R. W., 511, 522
Allen, A. H., 148, 163, 166
Allied Chemical & Dye Corp., 447, 497, 508
American Chicle Company, 668, 866
American Cholesterol Products Co., 332
American Cyanamid Company, 444, 491, 495, 496, 793
American Grease Stick Co., 755
American Gum Importers Association, 721
American Lignite Products Co., 369, 370, 807
American Museum of Natural History, 778, 856
American Resinous Chemicals Corp., 510, 882
American Rice Growers Coöperative Association, 237
American Society for Testing Materials, 603, 618
American Wax Importers and Refiners Association, 162
Ames, D. E., 46, 71
Amon, S., 192, 333
Anderson, R. J., 240, 241, 326, 327, 331, 333, 337, 338, 340
Anderson, Rudolph J., 43, 71, 308, 324, 325, 327, 330
Andes, L. E., 663, 865
André, E., 148, 634
Andreesen, G., 46, 71
Andrews, A. T., 856, 865
Andrews, E. D., 440, 442
Antonio Ajello & Bros., 656
Armour Chemical Division, 447, 478, 480, 482, 550, 551, 552, 555, 559, 579
Arnaud, A., 46
Arosenius, K. R., 43
Asano, M., 43, 46, 60, 71
Ashbutt, 166
Ashford, B. O., 869
Asiatic Petroleum Corp., 404
Asnes, Ben, 641, 868
Aswath Narain Rao, K., 222, 330
Atlantic Refining Co., 398, 503, 617, 619, 631, 632
Atlas Powder Company, 491, 495, 540, 855
Attapulgus Clay Co., 427
Auer, L., 498, 522
Ault, W. C., 141
Austermal Laboratories, Inc., 771
Austin, A. E. V., 890
Avequin, M., 218, 330
Axelrad, Sol., 546, 579
Aylsworth, J. W., 453, 495, 854, 865
Ayres, Jr., E. E., 126, 330

Bacon, C. V., 859, 870
Baczewski, 60
Bader, A. R., 74
Badische Anilin- & Soda-Fabrik, 451
Baer, Erich, 148, 330
Bagard, P., 44, 71
Bakelite Corporation, 508
Baker Castor Oil Co., 463, 471, 473
Baker, R. T., 244, 330
Balch, R. T., 221, 226, 227, 330
Baldeschwieler, E. L., 566, 579, 865
Baldinus, J. G., 191, 192, 193, 333
Bardorf, C. F., 224, 330
Bardwell, C., 353, 375
Bareco Oil Company, 428, 435, 441, 529, 530
Barenther, A., 301, 330
Baril, George, 98
Barkenbus, C., 65, 67, 75
Barnes, C. S., 135, 139, 330
Baron, C. E. H., 706
Barrett, A. W., 46
Barta, E. J., 743, 865
Bartels, H. J. M., 819, 865
Barth, E. J., 495
Batavian Petroleum Co. (Amsterdam), 442
Bateman, R. L., 449, 496
Baughman, W. F., 330
Baŀant, V., 256, 257, 333
Beard, R. E., 423, 441, 866
Beck, G., 7, 71
Becker, Max, 114, 120, 331, 333
Beckers, W., 690, 865
Beer, R., 43
Beiersdorf, Ltd., 642, 865
Beklemisheva, N. A., 865
Bell, H. S., 16, 71, 379, 441
Bell, S. A., 463, 464, 475, 495
Bellamy, L. J., 137, 330, 565, 579
Bellier, J., 99
Bell Telephone Laboratories, Inc., 696
Belluci, I., 481, 495
Benedikt, M., 127, 592, 593, 634
Benham, G. H., 589, 634
Bennett, Harry, 101, 331, 789, 865, 891
Benson, A. A., 6, 72
Benson, H. E., 467, 495
Bèrard, L., 169
Berg, R., 81, 90, 92, 93, 94, 98, 99, 191, 193, 331, 584, 634
Bergmann, Warner, 28, 34, 43, 46, 52, 71, 121, 331
Berk, S., 864, 865
Bernhard, K., 48, 71
Berthelot, Marcellin P. E., 548
Bertholett, M., 569
Bertram, S. H., 128, 134, 331
Berzelius, J., 142
Bessey, C. E., 331
Betrabet, M. V., 43, 250, 331
Bianchi, A., 208, 331
Biltz, W., 572, 579
Binaghi, R., 251, 331
Bishop, C. T., 259, 331

Bisson, C. S., 77, 78, 80, 98, 100, **331, 340**
Bjerregaard, A. P., 186, 190, 191, **333**
Blachly, F. E., **441**
Blade, O. C., 391, **442**
Blair, E. H., 236, **331**
Blaise, E. E., 46
Blake, J. T., 751, **866**
Blakemore, H. S., 198, 199, **338**
Bleyberg, W., 20, 34, 39, 43, 44, 66, **71, 73**, 91, 106, 107, **333**, 366, **375**, 494, **495**
Blount, B. K., 115, 120, **331**
Bodenstein, 46
Böhringer, C. F. & Söhne, 450
Boekenogen, H. A., **72**
Böttger, F., 17, **74**, 89, **336**
Bohrer, P., 491, 492, **495**
Bohrisch, P., 100, **331**
Boler, Petroleum Company, 504
Bolle, J., 43
Bolley, D. S., 310, 311, **331, 337**
Bolley, P. A., 142, 450, **495**
Bolton, E. R., **331**
Bolton, Ethel Stanwood, 773, **865**
Bontoux, E., 281, **331**
Borden, Jr., G. C., 784, **865**
Bougault, J., **72**, 246, 247, **331**
Bourdier, L., **72**, 246, 247, **331**
Bowen, F. E. W., 705, **865**
Bowman, R. E., 34
Braconnot, H., 323
Bradford, Corporation, 125
Bradley, T. F., **495**
Braude, Felix, 843, **865**
Braun, J. v., 18
Breuer, F. W., 365, **375**, 538, **579**
Breusch, F. L., 46, 60, **72**
Briese, R. R., **475**
Brigl, Percy, 12, 34, 43, **72**, 328, **331**
Brill, H. C., 98
"British Pharmacopoeia," 87
127, 140, 142, **331**, 402
Brod, L., 14, 43, 60, 66, **74**,
Brodie, B. C., 18, 43, 89, 91, 92, 106, 162, 168, 169
Broeg, C. B., 221, 226, 227, **330, 331**
Brooks, B. T., 60
Broughton, B. W., 60, **72**
Brower, Paul V., 807, **865**
Brown, D. S., 630, **635**, 882
Brown, J. B., **72**, 89, 90, 163, 165, 166, 167, 175, 180, 182, 190, 193, **332, 334**, 590, 593, 595, 629, **634**
Brown, K. B., 490, **495**
Browning, Jr., H., 251, 321, **337**
Brückner, F. v., 366, 368
Brunn, P. F., 209
Bruson, H. A., 130, **340**
Bryant, J. D., 826, **865**
Buchler, C. C., 388, 391, 404, 407, **441**
Buchner, George v., 81, 82, 83, 84, 85, 88, 93, 98, 190, 191, **331**
Buckley, G. D., 440, **495**
Buckman, Jr., A. F., 862, **865**
Bulatkin, Iliya F., 163, 169, **442**, 576, **581**, 891, 892
Bullock, W., 324, **331**
Bunger, W. B., 163, 166, 167, 234, 235, 236, **331**
Bunker, R. U., 218, **331**
Bunsen, R. W., 142
Burdet-Berthod, V., 406
Burgess, A. H., 761, **866**
Burrell, H., 493, **495, 496**
Burroughs, S. G., 801, **866**
Burrows, F. R., 705, **865**
Burrows, Joseph, 702, **865**
Burrows, J. G., 705, **865**
Butcosk, R. A., 579, 644, **865**
Butler, J. M., 518, **522**, 639

Cable, A. J., 789, **865**
California Forest and Range Experimental Station, 200
Calvert, W. C., 752, **865**
Calvin, M., 6, **72**
Campbell, M. R., **375**
Campbell, Sydney G., **338**
Canadian Industries Ltd., **496**
Canada Paper Company, 512, **523**
Carbide and Chemicals Company, 449
Carhart, H. W., **72**, **332**
Carleton, R. K., 283, **331**
Carlisle Chemical Works, 488
Carmody, W. H., 666, **865**
Carothers, W. H., 12, 14, 67, **72**, 468, 626
Carpenter, J., 12
Carpenter, J. A., 404, 411, **441**
Carson, C. C., 638
Carter, C. L., 145, **331**
Carvallo, Abel de, 79, **335**
Casimer, E., 36, **74**, 95, **335**
Cason, J., 43, 66, **72**, **74**, 325, 327, **331**
Casparri, W. A., 53
Casparis, P., 657, **865**
Catalino, E. L., 69
Cavanna, R., 43, **72**
Cawley, C. M., 358, 371, **375**
Central Waxed Paper Co., 790
C. G. Smith & Co., Ltd., 219
Chafejeu, 91
Chakravarti, G. C., 250, **331**
Charch, Wm. H., 795, **865**
Chargaff, E., 13, 325, **330**
Charles H. Phillips Chemical Co., 672, **866**
Chemische Werke-Hansa, 482, **495**
"Chemurgic Digest," 263
Cheremisinoff, P. N., 572, **580**
Chesebrough Mfg. Co., Consolidated, 677, **868**
Chesebrough, R. A., 418
Chevreul, M. E., 23, 33, 142, 546, 548
Chibnall, A. C., 34, **74**, 114, 167, 192, 193, 233, 245, 288, 329, **331**
Chigusa, L., 689
Chilikin, M. M., 201, 202, **331**
Chittenden, 60
Christensen, C. W., 480, **496**
Chuit, Philippe, 34, 46, 52, 54, **72**, 246, 247, **331**
Cities Service Company, 381
Ciusa, R., 345, **375**
Clare, I. C., 853, **866**
Clark, I. L., 260, 261, 262, **331**
Clarke, Carl D., 769, **866**
Clarke, E. W., 14, 16, **72**
Clarkson, C. E., 69, **72**
Clary, B. H., **441**
Clatcher, 221
Clayton, Wm., 652, **866**
Clewer, H. W. B., 321, **339**
Clotofski, E., 254, **332**
Cocceta, Sister M., **635**
Cohen, N. H., 31, **72**
Cohoe, W. B., 666, **866**
Cole, H., 839, **869**
Cole, Joseph, 645, **866**
Coleman, L. V., 776, 777, **866**
Collins, F. J. E., 20, 34, 38, **72**, 106, 107, **332**
Commercial Corporation, 429, 431
Conrad, C. M., 204, 205, **332**
Conrad, Lester I., 139, **332**
Consolidated Engineering Corp., 631, 632
Cook, A. A., 855, **866**
Cooke, Giles B., 258, **332**
Cooper, J., 293, **340**
Cooper, T. T., 105
Copley, C. J., **866**
Cordray, J. M., 844, **866**
Corkery, F. W., 522, **523**, 801, **866**
Cornwell, R. T. K., 795, **866**
Corrigan, John, 219
Cortese, D., 81, 98, **332**
Cothran, C. D., 738, 743, **866**
Cousins, E. R., 237, 238, **332**
Cowles, H. C., 413, **441**
Cox, W., 150, **332**
Cranberry Canners, Inc., 282
Crass, Jr., M. F., 765, **866**
Creighton, M. M., 326, **330**
Criswell, J. A. E., 767
Cross, C. F., 230, **332**
Cross, S. T., 866

Cross, W. E., 218, 225
Crowe, J. C., 229
Crown Cork & Seal Co., 607
Crown Zellerbach Corp., 642
Cuban-American Company, 224
Curbera, G. C., 258, 337
Curtis & Harvey (Tonbridge), 705
Czarnecki, J., 761, 870
Czerny, W., 73

D'Ambrosio, A., 72, 315, 316, 332
Damoy, G., 12, 43, 49, 69, 72, 89, 91, 92, 332, 333
Daniel, D., 137, 332
Darmstädter, F., 133, 134, 332
Daugherty, P. M., 185, 187, 188, 194, 304, 332
David, Aubrey D., 437, 441
David, S., 31, 72
Davidsohn, A., 745, 849, 866
Davidsohn, I., 745, 849, 866
Davies, L. A., 46, 72
Davis, C., 814, 815, 866
Davis, Carrol C., 751, 866
Davis, H. S., 452, 495, 646, 856
Dayton, W. A., 275, 334
De, C. C., 111, 332
Dearborn, F. E., 685, 856
De Bary, A., 151
Decepoli, C., 759, 866
De Coste, J. B., 866
Deffet, L., 33, 34, 39, 72
Deguide, H., 720, 866
Deiler, A. C., 189, 190, 191
De Keghal, Maurice, 842, 866
Delcourt, Mlle. Y., 12, 13, 20, 25, 72, 547, 580
Delmonte, J., 695, 866
De Navarre, M. G., 128, 142, 332
Dennis, F. L., 423
Deuel, Jr., H. J., 28, 43, 72, 323, 332
Diamond Alkali Company, 452, 868
Diamond Match Co., 764, 766
Dickinson, T. A., 186, 332
Dieterich, K., 100, 332
Dieterle, H., 100, 252, 269, 332
Diggs, S. H., 407, 423, 441, 697, 856
Dillon, Thomas, 359, 376
Dimter, A., 324, 322
Dispersion Process, Inc., 515
Dixson, W. H., 866
Dobbie, J. J., 840
Dodd, H., 866
Dodge Cities Industries, Inc., 235
Dodge, Lloyd L., 790, 866
Dominik, Z., 376
Donnely, J. T., 357
Doss, Eddie M., 385, 441
Dorinson, A., 39, 44, 72, 634
Doss, M. P., 580
Dover, M. V., 430, 441
Dow Chemical Company, 511, 737
Drake, B. L., 257, 258, 332
Dr. Fuchs & Co., 776, 866
Drekter, I. J., 139, 332
Drickamer, H. G., 389, 441
"Drug and Cosmetic Industry," 670
Duggan, W., 488
Dulk, 142
Dunlop, H., 144
Dupont, G., 258, 332
Dura Commodities Corp., 492, 498, 534, 725
Dutt, Sikhibhusan, 264, 297, 299, 332, 333, 337
Dutton, W. C., 532, 580, 844, 866
Dye, W. B., 80, 100, 331
Dyer, J. W. W., 20, 34, 66, 71

Eagle Pencil Company, 690, 866
Easterfield, T. H., 477, 495
Eastern Reginal Research Laboratory, 134
Eastman Chemical Products, Inc., 448, 499, 533
Easton, N. R., 735, 866
Eberlin, L. W., 761, 866
Ebert, M. S., 801, 869
Eckert, A., 312, 336
Edwards, R. T., 632
Egan, James, 373, 375
Eichorn, F., 163
E. I. du Pont de Nemours & Co., 446, 471, 472, 474, 496, 857, 868
Eisenlohr, G. W., 550, 580
Eisenreich, Kurt, 364, 367, 368, 375
Eisenstein, A., 43
Eisner, A., 140, 141
Ellern, H., 767, 866
Elliott, S. B., 580
Ellis, Carleton, 354, 355, 375, 554 567, 580, 852, 859, 866
Emery Industries Inc., 479, 496, 550, 579
Emlyn, J. A., 357, 376
Emmanuel, E. J., 98
"Encylopaedia Brittanica," 332
"Encyclopedia of Chemical Technology," 441, 580
Engel W. F., 493, 496
Engelhardt, R., 454, 455, 496
English Jr., J., 132, 340
Enjay Company, Inc., 505, 511, 803, 804
Ennis, E. C., 729, 734, 866
Epifanov, F., 72
Erchak, Jr., M., 446, 496
Erdle, R. W., 771
Ericks, W. P., 489, 496
Erlbach, H., 73
Erlenmyer, E., 258
Ernst, Carl J., 858, 867
Esso Standard Oil Co., 382, 502, 510
Evers, Norman, 145, 332
Ex-Cell-O Corporation, 502

Faber, H. A., 126, 332
Fairburn, W. A., 866
Fairweather, D. A., 52, 54, 72
Falqui, P., 251, 331
Farben Fabriken Bayer (Leverkusen), 458
Farbwerke Hoechst A. G., 459, 461
Farcy, L., 163, 169, 186, 189, 332
Farghet, R. G., 206, 207, 332
Farnham, H. M., 615, 634
Farrar, G. E., 869
Farrell, K. T., 735, 865
Fassbender, H., 731, 867
Fay, I. W., 576
Fayoud, A., 140
Feagin, Roy C., 773, 867
Felstein, L., 332
Fernholz, F., 30, 75
Ferris, S. W., 413, 441
Fetterly, L. C., 423
Feurt, S. D., 211, 289, 332
Fierz-David, H. E., 332
Fieser, L. F., 46, 72
Filemonewicz, C., 375
Findley, T. W., 72, 90, 163, 175, 180, 182, 190, 191, 332, 590, 593, 595, 629, 634
Fiore, A. J., 545
Fischer, Emil, 453
Fischer, Franz, 465, 553, 566, 567, 580
Fischer, H. O. L., 43, 148, 330, 496
Flaschenträger, B., 52, 72, 273, 332
Flaxman, M. T., 543, 580
Flint, G. W., 723, 724, 867
Flint, James E., 757, 867
Floridin Company, 427
Fontes, A., 324, 332
Food Machinery Corporation, 742, 869
Foote Mineral Company, 473
Forcey, C. W., 522, 691, 865
Fordyce C. R., 43, 46, 72
Forrest, C. N., 649, 867
Foster, E. O., 303, 333
Foster, H. J., 145, 332
Fourcroy, E., 569
Fourness, C. A., 863, 867
Fox, J. J., 840
Fox, L. E., 211, 332

Francis, F., 12, 20, 34, 38, 45, 52, 65, **72**, 405, **441**, 624, 633, **634**
Frank, A., 361
Frank Charmel, Inc., 683
Franke, Wilhelm, 475
Frankford Arsenal, 864
Franklin Research Company, 737, 741, 862
Fraps, C. S., 192, **332**
Freeman, H. G., 821, **867**
Frerichs, G., 143, **332**
Friedman, A. H., 467, **496**
Friedolsheim, Adolph v., **580**
Friedrich, Herman, 527, **580**
Frolich, Per K., 453, **496**, 646, **867**
Fugmann, R., 32, **73**
Fujita, A., 247, **333**
Fuld, Melvin, 724, **867**
Fuller, C. S., 697
Funk, C. S., 783

Gabrilovich, O. G., 99
Galle, E., **441**
Garcia Cruz, 191
Gargen, Otto F., 858, **867**
Gareis, M., 20, 24, **73**
Garner, W. E., 12, 20, 39, 43, **73**
Gascard, Albert, 12, 14, 20, 23, 34, 43, **73**, 89, 106, 113, **333**
Gaylor, P., **865**
Gebauer-Fuelnegg, E., **523**
Geist, G., **75**
Geller, L. W., 658, **867**
General Electric Co., **495**
Gentner, R., 39, 43, **73**
George, H. O., 812, **868**
German Pharmacopoeia, 85, 142
Giacomello, G., 316
Gibson, W. H., **74**, 201, 316, **333**
Gibson, W., **74**
Gilchrist, P. S. 468
Giller, E. B., 389, **441**
Gillespie, Rogers, Pyatt Co., 112
Ginger, G., 326, **333**
Girelli, A., 450, **496**
Gisvold, O., 215, **340**
Givaudau-Delewanna, Inc., 680
Glickman, C. S., 521, 522, **523**, 720, 824, **867**
Glyco Products Co., 487, 494, 537, 733
Göppert, 246
Goldon, E. H., 768, **867**
Goldreich, S., 848, **867**
Gomes, Pimental, **333**
Gomez, Justo, 163, 267
Gonzalez-Trigo, G., 297, 298, **333**
Goodman, H., 687, **867**
Goodyear Tire & Rubber Co., 511, 513, 514, 729
Gottfried, S., 12, **73**, 169, **333**
Gottlieb, O., 298, **334**
Govers, Francis X., 422, **441**
Gradnich, B., 818, **867**
Grate, L. G., 682, **867**
Graves, G. D., 388, 391, 404, **441**
Green, B. C., 815
Green, T. G., 60, **73**, 305, **333**
Green, S. J., 474, **496**
Greene, R. A., 303, **333**
Greenstreet, O. P., 737, **867**
Greer, C. M., 43
Greer, J. W., 727
Greig-Smith, Sydney, 323, **333**
Gresshoff, M., 242, 268, 269, **333**
Griesinger, W. K., 527, 528, **580**
Griffith, R., 739, **867**
Grimme, C., 281, **333**
Groat, R. A., 727, 845, **867**
Grodman, B., **333**
Groff, F., 512
Gross, Howard H., 426, **441**
Grün, A., 47, 52, **73**, **580**
Grün, A. D., 475, 481, **496**
Guillemonat, 256, **332**
Guiteras, A. F., 463, **496**
Gulf Refining Co., 428
Gupta, G. N., 222, 311, **330**
Gupta, M. P., 7, **333**
Gupta, S. S., 311, **333**
Guyer, Aug., 474, **496**

Haar, A. W., Van der, 289, **333**
Haas, Theo., 892
Haberlandt, G., 152
Hackman, R. H., 116, 119, **333**
Hammerlee, W., 279, **340**
Hall, W., 203, **334**
Halle, F., 52, **72**, 273, **332**
Haller, M. H., 740, 742, **867**
Halls, E. E., 454, **496**
Halpern, A., 687, **867**
Hamai, S., 466, 467, **496**
Hamilton, S. G., 576
Hamor, Wm. A., 458
Handy, J. O., 739, **867**
Hanford, W. E., 495, **496**
Hanzely, E. M., 225, **376**, 576, **581**
Happoldt, W. B., 693, **867**
Harding, T. S., 220, **333**
Hardwick, P. J., 151, **333**
Hare, R. F., 186, 189, 190, 191, **333**
Harper, Frank, 758, **867**
Harris, H. A., 859, **867**
Harrison, D. V., 630, **635**, 882
Harry, R. G., 681, **867**
Hartshorne, 390
Harwood, Jas., 488, **496**
Hata, Chuta, 88, **333**
Hata, T., 273, **333**
Hatt, H. H., 222, 223, **333**
Hattori, S., 808, **867**
Hausman, J., 357, **376**
Hausser, J., 46, **72**, 246, 247, **331**
Hauth, A., 598, **635**
Hawley, T. G., 720, **867**
Hawke, F., 278, **338**
Head, R., 853, **867**
Heckel, H., 466, **496**
Hefley, Dana G., 387
Heiduschka, A., 20, 24, **73**, 100, 128, 130, 136, **333**
Heilbron, I., 343, 344, **375**
Heim, F., 216, **333**
Heintz, W. von, 143
Heintz, W., 273, **336**, 560, **580**
Heisel, P., 368
Helfenberg, K. D., 97, **333**
Hell, C., 364, 367, 576
Helmers, C. J., 430, **441**
Henderson, L. M., **441**
Hendricks, S. B., 52, **73**, 289, **336**
Henriques, V., 106, **333**
Hengeveld, B., 224, **340**
Henricksen, Alfred, 387
Herbert, A., 216, **333**
Herbig, W., 196, **333**, **375**
Hercules Powder Co., 511, 891
Hergert, H. L., 60
Hermanns, O., 576
"Hermes," 697
Herr W., 254, **332**
Herschberger, Albert, 795, 866
Hett, 89
Hewer, D. G., **331**
Hewett, C. L., 139, **333**
Heyden Chemical Company, 538
Higginbotham, L., 207
Higgins, 201, **333**
Hilditch, T. P., 60, **73**, 147, 191, 201, 305, **333**, **375**
Hildebrand, J. H., 12, **73**
Hilfer, H., 192, **580**
Hill, J. W., **72**
Hinds, Wm. E., 819, **867**
Hintzer, H. M. R., 733, **869**
Hirai, H., 97, 97
Hirschler, H. E., 192, 202, **333**
Hocheder, F., **75**
Hochstadter, F., **579**
Höhnel, 258
Höhning, 387
Hoerr, C. W., 34, **74**
Hoffmeister, C., 202, **333**
Hoiberg, A. J., **869**
Holde, D., 39, 43, **73**, 91, 106, 107, **333**, 366, **375**, **634**
Holmes, A., 571, 576, **580**
Holmes, E., 38, 43, **74**
Hooker Electrochemical Co., 452
Hopkins, C. Y., **73**
Horn, D. H. S., 133, 136, 137, **333**
Horne, J. W., 374, **376**
Houghen, F. W., 136, 137, **333**
Houston, D. F., 46, **73**
Houston, J. F., 846, **867**
Houston, R., **867**
Howard, P. F., 126, **332**

Howe, C. C., 642, 867
Howe, I. S., 535, 580
Hubbard, J. K., 252, 253, 335
Huber, W., 338, 867
Huber, W. F., 73
Hugh, R. D., 269, 333
Hughes, C. M. C., 844, 867
Humacid Company, 807
Humboldt, von, F. H. A., 176
Humes, W. S., 493, 523
Huminski, W., 105, 106, 333
Humphrey, I., 60
Hunsdiecker, H., 63, 73
Hunter, J. H., 403, 853, 867
Huszi, K., 334
Hyde, J. B., 642

Iachan, A., 298, 334
Ibarra, H. P. Y., 81, 99, 335
Ibing, G., 468, 469, 496
Ichibe, A., 30, 73
I. G., Farbenindustrie Aktien-Gesellschaft, 223, 371, 454, 457, 458, 459, 460, 533, 565, 580
Ikeda, I. H., 213, 334
Ikuta, H., 96, 97, 99, 334
Imperial Chemical Industries, Ltd., 447, 457, 495, 496, 512, 523, 706, 866
Indian Refining Co., 441
Indian Lac Institute, 110
Ingle, Jas. D., 728, 730, 867
Inoue, S., 251, 334
Institute of Coal Research (Ruhr), 466
Interchemical Corporation, 868
Irimescu, I., 391, 442
Isely, C. C., 235, 334
Ishii, Y., 130, 131, 133, 134, 135, 335
Ishiwata, Y., 238, 334
Islip, H. T., 93
Itallie, van, E. L., 279
Ittner, Matin H., 549, 550, 580
Ivanovszky, Leo, 178, 233, 334, 714, 867
Iyer, S. N., 44

Jacini, G., 20, 73, 212, 243, 334
Jacobsen, J. J., 301, 334
Jacobsen, Robt. P., 257, 333
Jacobson, C. A., 571, 576, 580
Jahrstorfer, Michael, 364, 376, 458, 461, 496
Jamieson, G. S., 73, 304, 307, 334, 335
Janer, J. R., 741, 868
Jasinski, J. v., 843, 867
J. C. Johnson & Son, Inc., 742
Jeger, C., 32, 74
Jehlicka, G. F., 85
Jensen, W., 255, 334
Jermstad, A., 280, 334
Jessen, C. C., 863, 868
John Eisenbeiss Corp., 648
Johannes, Jr., D. B., 862, 868
Johnson, J. R., 42, 72
Johnson, R. A., 639
Johnson, Robt. I., 652
Jonas, K. G., 5, 73
Jones, Lee D., 425, 441
Jones, R. G., 20, 45, 65, 66, 73
J. Spicer & Sons, 868

Kale, E. W., 867
Kalish, J., 673, 868
Kallander, Ernest L., 641, 868
Kamolova, L. D., 202, 331
Kariyone, T., 334
Karlik, B., 468
Karrer, P., 18
Kawakami, Y., 334
Kawasaki, Toshio, 60
Kazda, J., 747, 868
Kebler, Lyman F., 89, 142, 334
Kellermann, August, 734, 868
Kelley, W. Carl, 821, 868
Kelly, E. G., 597, 635
Kelsey, H. D., 275, 334
Kerschbaum, M., 52, 73
Keskin, H., 46, 72
Kettering, J. H., 205
Khan, M. Hanif, 181
Khorana, M. L., 245, 336
Kiawaga, F., 328, 334
Kiefer, H. J., 260, 261, 335
Kiesel, Alex., 73
Kiessig, H., 160
King, A., 693
King, A. M., 14, 34, 45, 72
King, J., 732, 865
King, J. G., 353, 371, 375
Kirk, R. E., 868
Kissling, R., 604, 634
Kitson, R. E., 623, 635
Kitsa, E. D., 175, 176
Kium, T. P., 335
Kjellstrand, A. G., 311, 868
Klee, L., 589, 634
Klaiderer, C. W., 607
Kleinstück, 271
Klenk, E., 60, 73, 323, 329, 334
Klimont, J., 572, 576, 580
Knaggs, Nelson S., 110, 175, 178, 179, 185, 186, 187, 211, 334, 774, 868
Knecht, E., 203, 204, 205, 207, 334
Knoepfler, G., 640, 868
Knol, N. V., 136, 334
Knowles, C., 426, 441
Knowles, Edwin C., 426, 441
Knuth, E. H., 753, 868
Koch, Herbert, 468, 469, 496
Koch, J. R., 625
Koch, William, 519, 520, 523
Koehler, A., 46
Kösters, O. A. H., 482, 496
Komori, S., 34, 73,
Kono, Michio, 17, 66, 73, 114, 115, 116, 118, 119, 120, 334
Koome, J., 493, 496
Koonce, S. D., 165, 166, 167, 334
Koppers Company, 440
Korb-Pettit Wire Fabrics and Iron Works, 738
Koster-Keunen Co., 86
Kovács, E., 12, 34, 43, 74, 95, 335
Koyama, R., 43, 69, 107, 108, 116, 117, 118, 311, 334
Kozlov, N. S., 15, 73
Krafft, F., 34, 43, 52, 64, 69, 73, 405, 441
Kramer, Henry, 344
Kranz, H., 17, 18, 74, 116
Krczil, Franz., 496
Kreger, D. R., 7, 9, 23, 73
Kresling, K., 324, 335
Kreutzer, A., 366, 367, 368, 376
Krewson, C. F., 65, 66, 73
Kroner, A. A., 720
Kroppscott, E. L., 521, 523
Krupp Kohlechemie G.m.b. H., 486, 534, 791
Kubo, H., 309, 338, 464, 496
Kuchinka, R., 554, 565, 567, 580
Kügler, 258, 335
Kuhn, E., 96, 335
Kuhrt, N. H., 536, 580
Kummerow, F. A., 163, 166, 167, 234, 235, 236, 331, 335
Kunisaki, T., 273, 333
Kunz, E. C., 545
Kurth, E. F., 60, 252, 253, 260, 261, 335
Kurts, Jr., E. B., 216, 234, 269, 317, 335
Kutono, M., 335
Kuwata, T., 130, 131, 134, 135, 335

Lach, B., 126, 335
Lang, Louis, 734, 869
Langenhagen, Gustav, 747, 868
Langmuir, Irving, 37, 73
Lapal Studios, 656
Lardelli, G., 74
Latham, Geo. H., 706, 869
Laufer, R. E., 868
Laurant, 453
Lauro, M., 572, 573, 576, 581
Lawrence, A. S. C., 571, 572, 576, 580
Lawa, E. Q., 151, 333
Leader, W. M., 546, 580
Lech-Chemie Gerstbofen, 368
Lederer, E., 137, 322, 335, 340, 360, 375
Lederer, Ph., 349, 360, 375

Lee, J. A., **335**, 622, **635**, 700, 701, **868**, 890
Lees, P. M., 81, 99, **335**, 345, **375**
Legg, V. H., 209, **335**, 345, **375**
Lepierre, C., 79, **335**
Lesser, M. A., 710, **868**
Le Sueur, H. R., 46, **74**
Lesuk, Alex., 326
Levene, P. A., 12, 14, 20, 34, 43, 65, 66, **74**, **75**, 328, **335**
Lever Brothers, Inc., 685
Lewkowitsch, J., **74**, 89, 91, 104, 122, 163, 165, 169, 258, 264, 300, 324, **335**, 555, 560, **580**, 591, 595, **635**
Leys, Alex., 89, 91, 92, 166, 190, **335**, 595, **635**
Libby, S. W., 642, **867**
Libovitz, Hyman, 831, **868**
Licata, F. J., 575
Lieber, Eugene, 645, 646, **868**
Liebermann, C., 114, **335**, 597
Liebig, Justus, 142
Lifschütz, M., 133, 134, **332**
Lindgren, B. O., 5, **74**
Linnaeus (Linné, Carl von), 76
Lion Oil Company, 643
Lipp, A., 12, 34, 36, 43, **74**, 95, 96, **335**
Lipson, M., 134, **335**
Lockermann, G., 655
London Shellac Research Bureau, 111
Loon, van J., 291, **338**
Lorentz, H. A., 634, **635**
Lorenz, L., 634, **635**
Louveau, G., 315, 317, 318, 321, **335**
Lovell, S. P., 516, 754, 773, **868**
Lovern, J. A., 147, **333**, 343, **375**
Lowden, W. P., 487, 694, **868**
Lowe, E., 743, **865**
Lower, E. S., 141, **335**
Lowry, H. H., 632, **635**, 700, 701, **868**, 890
Lubricol Sales Corporation, 451
Luciani, J., 705, **868**
Luckè, B., 326
Luddy, Francis E., 597, **635**
Lüdecke, C., 43, 180, 189, 190, 210, 231, **335**
Lüscher, E., 257, **341**
Lukeš, R., 46
Lummus Company, The, **523**, **870**
Luther, M., **580**
Lux, H., 712, **868**
Lycan, W. H., **74**

Mabery, C. F., 388, 391, 404, **441**
McBeth, C., 112, 199, 200, 309, 329, **336**, 892
McClelland, C. P., 449, 486
McClenahan, W. S., **868**
McCorkle, M. R., 39, **72**, **634**
McCormack, R. H., 310, **331**
McDonnel, M. E., 832, **869**
Macek, T. J., 818, **868**
McElvain, S. M., 475
Machado, A. A. de Souza, 181, **335**
Machek, V., 369, **375**
Mack, W. B., 741, **868**
McKay, A. F., 43, **74**, 276, 277, **336**
McKinney, R. S., 304, **336**
MacLaren, F. H., 409, **441**, 792, **865**
Macleod, J. J. R., 324, **331**
McLoud, E. S., 221, **336**
Madeiros Transcoso, A., de, 174
Maille, M., 634
Majumdar, V. P., 853, **868**
Maksimova, S. N., **575**
Malatesta, G., 208, **331**
Mallinckrodt Chemical Works, 573
Malkin, T., 34, 66, 69, **72**, **73**, **74**
Malstrom, I., 127, **340**
Manley, R. E., 383, **441**
Mansaroff, A., 573, **580**
Marathon Paper Mills Co., **865**
Marbon Corporation, 513, **523**
Marcelet, H., 280, **335**
Marcusson, 17, **74**, 89, **335**, 355, 360, 361, **375**, 387, **442**, 584, **635**
Marie, T., 96, **336**
Marion, L., 28, **74**
Markley, K. S., 34, 38, 43, 46, **74**, 174, 289, 290, 299, **336**
Markwood, L. N., 303, 306, **336**
Marran, J. S., 812, **868**
Marsel, C. J., 162, 163, 164, **336**, 462, **496**, **580**
Marshall, A. W., 434, 608, **635**
Martell, P., 98
Martin, G., 147, **336**, 660, **868**
Maruyama, R., **73**, 114, 116, 119, 120, **334**
Marwedel, J., 112, **336**
Masami, O., 121, **336**
Mason, C. W., 406
Mason, R. G., 34
Matsuda, J., 228, **336**
Matthes, H., 249, 273, **336**
Mattil, Karl F., 39
Matumoto, I., **75**, 89, **340**
Mauro, O. G., 385, **441**
Maxfield, L. I., 353, **375**
Mayer, C. W., 809, **868**
Mazee, W. M., 12, 14, **74**, 389, 405, 406, 413, **442**
Meara, M. L., 311, **333**
Meier, K., 592, 593, **635**
Meier, Karl, 166, **336**
Meisels, A., 32, **74**
Meldrum, R., 142, **336**
Mellon Institute, 449, **495**
Menzies, A. W. C., 628, **635**
Merck and Company, 818
Mertens, W., **74**
Messer, W. E., 18
Metasap Chemical Co., 573, 574, **580**
Metayer, L., 419, **442**
Metcalf, Woodbridge, 199
Meyer, Erich, 676, **868**
Meyer, E. W., 687, **865**
Meyer, H., 12, 14, 43, 60, 66, **74**, 102, 312, **336**
Meyer, J. D., 20, **74**
Meyerheim, G., 360, 366, **375**
Mill, R. J., **868**
Millar, C. C. H., 854, **868**
Miller, S. E., **75**
Mills, V., 373, **375**, 550, **580**
Minchin, S. T., 405, 406, **442**
Mink, L. D., 728, **867**
Mirov, N. T., 302, **336**
Mitchell, Jr., L., 628, **635**
Mitra, C., 322, **336**
Mitsui, T., 227, 228, **336**
"Modern Packaging," 787
Modi, P. K., 245, **336**
Molinari, E., 343, 348, **375**
Mollan, R. M., 119, **336**
Monick, J. A., 12, 34, 39, 44, 65, 66, **74**
Monsanto Chemical Company, 511, 639, 749, 838, **868**
Monsaroff, A., 576, **580**
Montagna, W., 329, **336**
Monti, L., **336**
Moore & Monger, Inc., 506
Moore, A. E., 710, 825, **868**
Moore, C. W., 290, **336**, **337**
Moore, F. G., 642, **865**
Moore, J. E., 802, **868**
Moos, Josef, 892
Moran, Robt. C., 644, **868**
Morgan, G. T., 38, 43, **74**
Morris, W. N., 283
Morton, J. L., 812, **868**
Mozingo, R., **72**, **332**
Müller, 142
Müller, Alex., 13, 37, **74**
Muhr, A. C., **338**
Mulcahy, 358
Muller, O. F., 543, **580**
Munising Paper Company, 639
Murphy, T. F., 814, **868**
Murray, K. E., 20, 43, **74**, 136, 165, 166, 167, 168, 169, **336**
Murti, P. B. R., 135, 211, 264, 296, 322, **336**
Musgrove, O. C., **336**
Myddleton, W. W., 46
Myers, L. D., 442

Nabenhauer, F. B., 240, 241, 248, **337**
Nafzger, Fr., **74**, 91
Nagel, W., **74**
Nakajima, A., **75**
Nakamori, E., 311, **337**
Nascimento, R. C., 293, **337**
Nash, A. W., 408
Nathan, C., **867**
National Bureau of Standards, 710, 778
National Cash Register Co., 815, **866**
National Oil Products Co., **867**
National Petroleum Association, 601
Navarre, M. G. de, 681, **868**
Nealy, Walter A., 282, 293, 287, **331**, **337**
Neely, J. W., 204, **332**
Neiditch, Sam. A., 809, **868**
Nelson, H. A., **868**
Nenitzescu, C. D., 39, **442**
Neumann, Richard, 375, **375**
Neville Company, 511
Newberg, R. G., 803, **869**
Newburger, S. H., 677, **869**
Newhall, J. F. P., 741
Niemann, Albert, 213
Niemann, C., 18, 64, **74**
Nier, E., **73**, 128, 130, 136, **333**
Nillson, K. T., 565, **579**
Nikitina, E. A., 575
Ninomiya, M., 236, 325, **340**
Nishimoto, Y., **337**
Nishimura, M., **337**
Nitsche, K. S., 351, **375**
Nobori, H., 311, **337**
Noerdlinger, H., 52, **73**
Noncle, Maurice G. G., 527, **580**
Normand, A. R., 52, **74**
Normann, Wilhelm, 474, **496**, 592, **635**
Nozoe, T., 131, 133, **338**

Obata, Yatara, 280
O'Connor, R. T., 34, **74**
Ode, W. H., 360, 365, 369, **375**
Ogawa, G., 107, 240, **341**
Ogg, C. L., 593, **635**
Ohta, Jisaku, 43, 46
Olsen, A. B., 810, **869**
Olshausen, J., 648, **869**
Olsson-Seffer, Pehr, 190, 191, 277, **337**
O'Neal, Jr., M. J., 631
O'Neill, E. C., 759
Oregon Wood Chemical Co., 259
Osol, A., **869**
O'Sullivan, C., 357
Osumi, S., **334**
Othmer, D. F., **858**
Ottemann, L., 482, **496**
Overbaugh, W. V., **426**, **441**
Ozokerite Mining Co., 353

Pacius, Oscar, 186
Padgett, F. W., 387, **442**, **869**
Page, I. H., 329, **337**
Page, Jr., J. M., 411, 421, 423, **441**, **42**, **866**
Palmer, W. H., 703, **869**
Paraskova, V., 46
Pardun, H., 554, 565, 567, **580**
Paris Gum Corp. of America, 667
Parker, C. J., 751, **869**
Parker, M. E., 757, **869**
Paula, R. D., deG., 214, **337**
Pawleski, B., 350, **375**, 691
Pearsall, D. E., 704, **869**
Pease, F. N., 832, **869**
Pedersen, J. D., 707, **869**
Pegorari, Carlo, 211, **337**
Pekkering, J. J., 733, **869**
Pelza, N., 890
Pendse, Gajanan P., 264, **337**
Pentzer, W. J., 741, **869**
Penzio, G., **74**
Periotte, R., 46
Perrin, M. W., 447, **496**
Person, 142
Pescheck, G., 37, **75**
Petroleum Specialities, Inc., 416
Petrolite Corporation, Ltd., 428, 432, 504, 529, 718, 822, 830
Petrov, A. D., 475, 476, **496**
Pfaff, J. K., 360, 366, 367, 368, **376**
Pfaff, K., 845, **869**
Phillips Petroleum Company, 467
Picard, C. W., **337**
Pichard, G., 288, **337**
Pickett, O. A., 891
Picon, M., 575
Piraerts, J., 282, **337**
Pigulevski, G., 60
Pilt, 348
Pink, R. C., **75**, 576
Piper, J. D., 575, 576, **580**
Piper, S. H., 20, 34, 38, 65, **72**, **73**, **74**, 193, 233, **331**, 624, 633, **634**
Pirelli-General Cable Works, Ltd., 698, **869**
Pitman, N. J., 487
Plechner, W. W., **580**
Poell, H., 422, **442**
Polgar, W., 326, **337**
Politzer, W., 209, 210, **337**
Pollard, A., 233, **337**
Pontonié, H., 344, 357, **376**
Pool, Wm. O., 34, 39, 43, **74**, 488, **496**
Poole, J. W., 891
Porges, Philipp, 375, **375**
Porter, A. B., 126, **337**
Potonié, H., 357, **376**
Potter, P. B., 512
Potts, W. M., 310, 311, **337**
Pouillet, 142
Power, F. B., 34, 43, 251, 290, 321, **337**
Prakash, I., 297, 299, **332**
Prandi, O., 295, **337**
Prange, C. H., 771
Prelog, V., 20
Presting, W., 576, **580**
Price's Candle Factory, 399
Prince, Jr., L. M., 723, 724, **869**
Probert, M. E., 206, **332**
Productos Quimicos y Vegetales, S.A.I.C., 197
Proell, W. A., 859, 860, **869**
Prophéte, H., 314, 315, **337**, 360, 366, 368, **376**
Prout, F. S., 43, **72**, **74**, 325, **331**, **337**
Pschorr, R., 360, 366, 367, 368, **376**
Pummerer, R., 17, 18, **74**
Pungs, W., 364, **376**, 458, **496**
Pusey, Joshua, 767
Putambekar, S. V., 522, **523**

Quaker State Oil Refining Co., 436, 502
Quartermaster Corps of the U. S. Army, 736, 758, 800

Rabak, W., 786, 787, **869**
Radcliffe, L. G., **74**, 163, 318, 319, **337**
Radell, J., 134
Radio Corporation of America, 487
Ragon, P., 43
Rainer, Wm. C., 163
Ralston, A. W., 20, 25, 34, 39, 43, 46, **72**, **74**, 480, **496**, **534**
Rakshit, J. N., 296, **337**
Ramos, F., 293, **337**
Rangaswami, S., 94, 321, **337**
Rao, N. V. S., 296, **336**
Raoul, W., 214, **337**
Rather, J. B., 192, **332**
Rau, Karl, 428, **442**, 655, **869**
Rauhala, V. Y., 358, **376**
Ray, N. H., 446, **495**
Riebeck Montan Works, 362
Redgrove, H. S., 684, **869**
Reed, R. K., 798, **869**
Reeves, R. E., 327, **337**
Reichenbach, 401
Reichert, J. S., **337**
Reid, E. E., 20, **74**, 150, **222**, **332**
Reiff, O. K., 453, **496**, 640, 647, **869**
Reifsnyder, Jas. D., 797, **869**
Reilly, Joseph, 357, 358, **376**
Reindel, F., **74**
Reistle, C. E., 391, **442**

Remington Arms Company, 706, **869**
Rendall, M. M., 862, **865**
Resinous Products & Chemical Co., 444, 487
Rey, E., **338**
Reyes, D. Gil, 143, **337**
Reynolds Metals Company, 638
Rheinboldt, H., 69, **74**
Rhinelander Paper Co., 638
Rhodes, F. H., **337**, 406, **442**
Ribas, I, 258, **337**
Riebeck Montan Works (Germany), 360, 361, 362, 366, 459
Rindl, M., 278, **337**
Rivera, S., 140
Rivière, G., 288, **337**
Roberts, E. G., 327, **330**
Roberts, O. D., 98, 327
Robinson, G. M., Mrs., 20, 34, 43, 46, 66, **74**, **75**
Robinson, R., 34, 43, 46, 66, **74**
Rocca, J. P., **523**, **869**
Röhrs, W., 572, **579**
Rogers, L. F., 801, **869**
Rogers, T. H., 753
Rogerson, H., 206, 319, **337**, **338**
Roland, J. R., 495, **496**
Romins'kii, I. R., 363, **376**
Root, A. I., 103, **338**
Root, E. R., 103, **338**
Root, Huber, H., 87, **338**
Roquette, R., 357, **376**
Rosen, H. R., 755, **869**
Rosenkranz, G., 31, **75**
Rothstein, B., **75**
Rouvé, A., **75**
Ruben, S., **75**
Rubinstein, V., **580**
Rudloff, v., 136
Rudy, H., 320, **337**
Rüdorff, 142
Ruhrchemie, A.-G., 466, **493**
Rushbrooke, J. E., 20
Russel, R., 230, **332**
Russel, Robt. P., 149, **338**
Ruzicka, L., 20, 31, 32, **74**, **75**, 130, **338**
Ryan, Hugh, 85, 98, **338**, 359, **376**
Ryan, L. W., **580**
Ryder, E. A., 39, **73**

Sabetay, S., 319, **338**
Sachanen, A. N., 377, **442**
Sack, J., 242, 268, 269, **333**
Sada, Luis, 650
Sadtler, S. P., **340**
Saginaw Match Co., 764
Sajak, Emil, 749, **869**
Sakhanov, A. N., 388, **442**
Sakurada, I., **75**
Sakurai, Z., 248, **338**
Salamon, M. S., 98, 99
Sandberg, R. W., 815
Sanders, J. M., 189, 190, 191, 193, **330**, **338**
Sando, C. E., 286, 288, 289, **336**, **337**, **338**
Sankarasubramian, S., **337**
Sauer, J., 69, **75**
Saussure, 142
Sawyer, M. F., 408, **442**
Sayre, J. W., 467, **496**, **580**
Scalione, C. C., 198, 199, **338**
Scanlan, J. T., 141, 597, **635**
Schaal, Richard, 52, **75**, 272, **338**
Schade, C., 490, **496**
Scheithauer, W., **376**
Schilling, A. A., 706, **869**
Schlegel, J. W., 734, **869**
Schmidt, A. W., 18
Schmidt, W. J., 102, **338**
Schneider, A. K., 34, 43, 46, **75**
Schneider, H. G., 510, **523**, 802, **869**
Schneider, W., 553, 566, 567, **580**
Schoch, E. P., 204, 207, **339**, 891, 892
Schoeman, D. J., 278, **338**
Schoenfeld, R., 20, 43, **74**, 135, 136, 165, 166, 167, 168, 169, **336**
Schon, L., 20, **75**
Schreffler, C. B., 861, **869**
Schreiner, O., 323, **338**
Schroger, A. W., 211, **338**
Schuhbarth, 142
Schuette, H. A., 20, 34, 37, 46, **75**, 181, 190, 191, 192, 193, **338**
Schuh, C. H., 553, **869**
Schulz, F. N., 120, **338**
Schulze, G., 329, **338**
Schumann, E., 329, **334**
Schunck, Edward, 203, 205
Schur, M. O., **869**
Schwalb, F., 89, 92, 576
S. C. Johnson & Son, Inc., 182
Schwarte, Geo., 458, **496**
Scmuszkovics, J., 46, **72**
Scott, S. L., 489, **496**
Scripture, Jr., E. W., 514, **523**
Scurti, F., 255, 257, 258, **338**
Sebelien, J., 98
Seil, H. A., 839, **869**
Selvig, W. A., 360, 365, 369, **375**
Semet-Solvay Petrochemical Division, 447, 508, 533, 881
Sen, D. L., **330**
Serwy, H., 52, **75**
Seshadri, T. R., 211, 264, 322, **336**
Seubert, R. F., 440, **442**
Seydel-Wooley & Co., 527
Seymour, D. E., **337**
Shapiro, Abraham, 823, **869**
Sharma, Jagan N., 736, 738, 740 **869**
Sharpless Specialty Co., **441**
Shearon, Jr., W. H., **869**
Shell Corporation, 440, 882
Shell Development Co., 423, 473, 865
Shell Oil Company, 882
Shestakov, P. I., 46, **75**
Shiina, S., **338**
Shinosaki, Y., 69, 309, **338**, 404, **496**
Shriner, R. L., 43, 307, **338**
Shuger, L. W., 826, **869**
Siddiqui, S., 322, **336**
Siina, Sitiro, 52, **75**
Simmons, R. E., 219
Simonova, N., 60
Sinclair Refining Co., 503
Singh, P., 112, 338
Singleton, W. S., 35, **75**
Siniramed, C., 450, **496**
Sinozaki, Y., 481, **496**
Sirahama, K., 343, **376**
Skinner, E. W., 778, **869**
Skopnik, A. V., **335**
Slater, L. E., 727, 728, **869**
Smelkus, H., 361, 368, **376**
Smith, F. v. M. H. G., **338**
Smith, H. E., 643
Smith, H. G., 244, **330**
Smith, H. W., 688, **870**
Smith, L. H., 145, **338**
Smith, R. W., 512
Smith, Warren Rufus, 276, **338**
Snell, Foster D., 463, **496**
Snyder, J. E., 515, **523**
Socony Mobil Oil Co., 400, 664
Sonderegger, G., 258, **341**
Sorenson, Eric, 702, **870**
Sorm, F., 256, 257, **338**
Sosa, A., 215, 216, **338**
Soyka, Walther, 12, 14, 43, 60, 66, **74**, 192, **336**
Sparks, W. J., 508, 509, **523**
Spielman, M. A., 34, 43, 46, **75**, **325**, **338**
Spitz, 387
Stage, H., 147, **338**
Stainsby, W. J., 60, 305
Ställberg-Stenhagen, S., 15, 19, 22, 43, **72**, **75**
Stambaugh, R. P., 488
Standage, H. C., 840, **870**
Standard Oil Company (Indiana), 408, 421, 424, 428, **441**
Standard Oil Company (New Jersey), 396, 659, **870**
Standard Oil Development Co., **580**, 616, 646, 804, **870**
Steele, L. L., 643, **870**
Stefanowski, W., **376**
Stegeman, Gebhard, **442**
Stegemyer, L. A., 484, **496**
Steger, A., 291, **338**
Steinberger, S., **580**

Steinle, J. V., 46, **75**, 161, 211, **338, 496**
Stenhagen, E., 15, 19, 43, 46, **75**, 326, **338**
Stenhagen, S., 326, **338**
Stenhaus, 142
Stetten, DeWitt, Jr., 6, **75**
Stetten, M. R., 6, **75**
Stickdorn, Kurt, 362, 363, **376**
Stingley, Dale V., 555, **581**
Stobbe, H., 4, **75**
Stock, Erich, 109, **338**
Stockfleth, A., 693, **867**
Stocks, H. B., **376**
Stodola, F. H., 326, **338**
Stoll, M., **75**
Stossel, E., **339**
Straman, F. J. S., 315, 316, 318, 320, **339**
Straus, F., **75**
Straw, H. H., 773, **868**
Streat, G. H., 204, **334**
Streicher, L., 249, **336**
Stremme, H., 346, **376**
Stürcke, H., 165, 166, 169, **339**
Stürcke, L., 43, 168, 169
Suess, Albert, 697, **867**
Sumner, Cyril G., 652
Sun Chemical Corporation, 498
Sundgrén, A., 358, **376**
Sundwik, E. E., 43, **75**, 102, 206, **339**
Sun Oil Company, 382, 384, **502**
Sure-Seal Corporation, 732
Sutton, W. R., 406
Suzuki, Kozo, 43
Sweet, D. F., 163, 173, **339**
Swenson, O. J., 221, **337, 339**
Swett, A. P., 748, **870**
Swift, A. N., 34, 43, 52, **71**
Swietoslawski, W., **635**
Szmuszkovics, J., 46
Szwarc, A., 512, **523**

Tägström-Eketorp, B., 43, **75**
Takeshita, Y., **339**
Tamura, S.m **339**
Tange, Ume, 241, **339**
Tanret, C., 29
Tasaki, S., 318, **339**
Tassily, M. E., 272, **339**
Taub, Harry, 167, 236, 300, 407, **442**, 463, 464, **495**
Taylor, C. M., 477, **495**
Taylor, F. A., 20, 34, 43, 60, 65, 66, **74, 75**
Tears, C. F., 425, **442**
Teng-Han Tang, **339**
T. F. Washburn, Inc., 530, 710
Thacker, N. A., 814, 815, **866**
Thaler, H., **75**
Thiele, F. A., 687, **870**
Thierfelder, H., 328, **334**
Thies, H. R., **523**
Thomas, Gordon C., **523**, 804, **870**
Thomas, R., 685, **870**
Thompson, H. P., 769, **870**
Thomson, 89
Thorpe, Sir Edward, 183, 184, 278, **339**, 705
Tiedt, J., 43, 133, 134, 135, 136, **339**
Tilgman, 548
Tisot, P. R., 374, **376**
Tomecke, C. G., **75**
Tommasi, G., 255, 257, 258, **338**
Tonn, Jr., W. H., 204, 207, **339**, 891, 892
Tower, G. S., 677
Towner, J. C., 739, **870**
Toyama, Y., **75**, 97, 146, **339**
Transcoso, A. de Medeiros, 174, **339**
Tressler, D. K., 480, **496**, 787, **870**
Tropsch, Hans, 366, 367, 368, **376**, 465
Trusler, R. B., 787, 863, **870**
Truter, E. V., 43, 133, 135, 136, **339**
Tschesche, R., 32, **75**
Tsuchikawa, H., 273, **339**
Tschirch, A., 100, 152
Tsuchihashi, R., 273, **339**
Tsuchiya, T., 239, 241, **339**
Tsujimoto, M., 52, **75**, 272, **339**
Tsutsumi, S., 241, **339**
Tughan, V. D., **75**, 576
Tullie, Russell & Company, Ltd., 230
Tulus, R., 60, **72**
Tunman, 255
Turner, Jr., A., 597, **635**
Turner, W. R., 615, 630, **635**, 881, 882
Tutin, F., 34, 43, 321, **337, 339**
Tuzimoto, M., 243, **339**
Twitchell, Ernst, 549

Ueno, D., 34, **73**, 99, 240, 241, 242, 273, **339**
Ujhelyi, E., 348
Ulbrich, E., **496**, 554, **580**
Ullmann, F., 108, 142, 148, 149, 190, **339**
Ulrich, C., **332**
Ulrich, H., 20, 34, 39, 44, 66, 71, 257, 494, **495**
Ultée, A. J., 268, 269, **339**
Ulzer, F., 12, **73**, 169, **333**, 593, **634**
Underwood Elliott-Fischer Co., 809
Union Carbide and Carbon Corp., 456, 512
Union Oil Company, 382, 416
United Chemical Works (Charlottenberg), 85
U. S. Bureau of Mines, 369, 374, 466
U. S. Dept. of Agriculture, 786
U. S. Dept. of Commerce, 182, 219, 334, 460, **580**
"U. S. Dispensatory," 105, **340**, 815, 817
U. S. Industrial Chemicals Co., 511
"U. S. Pharmacopoeia," 84, 127, 142, 144, **340**, 402, **442**, 511, 558, 669, 687, 816, 817, 819, **870**
Utz, F., 128, **340**

Valenta, E., 169, **340**
Vallernaud, P. A., **340**
Van Beckum, W. G., 262, **340**
Van der Haar, A. W., 289, **333**
Van der Wielen, P., 819, 820, **865, 870**
Van Horn, H. T., 665, **870**
Van Natta, F. J., 67, **72**
Van Riel, Jr., 820, **870**
Vansell, Geo. H., 77, 80, 98, 100, **331, 340**
Varlamov, V., 567, **581**
Vauquelon, 176
Velick, S. F., 132, 325, **340**, 387
Velluz, L., 137, **332, 340**
Veneklasen, P. S., **870**
Venton, C. B., 223, **340**
Verkade, P. E., 20, 293, **340**
Vesterberg, R., 269, **340**
Viard, M. J., 314, 316, 317, 318, 320, **340**
Vogel, F. M., 100, **333**
Vogel, H., 37, **75**
Voightman, E. H., 863, **867**
Von Boyen, E., 361, 362, **376**
Von Humboldt, Alex., 176

Wachter, A., 12, **73**
Wade, F. B., 276, **338**
Wade, S. E., 838, **870**
Waentig, P., 37, **75**
Wagner, C. D., 64, **74**
Wagner, E. F., 577, 578, **581**
Wagner, C. L., **522**, 803, **865**
Wagner, H., 312, **340**
Wall, M. E., 244, 597, **635**
Waller, C. W., 215, **340**
Wallingford, R. W., 405
Wallis, E. S., 30, **75**
Walker, P. H., 643, **870**
Walmsley, W. N., 159, **340**
Walsh, C. L., 209, **340**
Walter, Robt., 367, **376**, 576, **581**
Walton, B., 672, **870**
Wand, M., 585, **635**
Warming, E., **340**

Warp, H., 512, **523**
Warth, A. H., 163, 199, 200, **329**, **340**, **376**, **442**, 576, 581, 710, **870**, 891, 892
Warth, Jr., 112, **340**, **870**
Warwick Wax Company, 229, 429, 529, 807
Was de Witt, N. V., 112
Wassermann, R., 732, **870**
Watkins, C. M., 305
Watson, N. A., **870**
Waxed Paper Institute, 770
Weber, E., **340**
Weihe, Jr., F. A., 726, **870**
Weil, M. A., **870**
Weingaertner, A., 427, **442**
Weinlagen, A. B., 241, **340**
Weir, Jr., T. P., 631
Weitkamp, A. W., 43, 130, 131, 135, 163, 167, **340**
Weitzel, 43
Welch, T. H., 830, **870**
Wells, F. B., 306, **340**, 643, **870**
Wendland, J. C., 176
Wendt, R. E., 577, 578, **581**
Werk Lech-Chemie Gersthofen, 459, 461, 525
West, C. J., 14, 43, **74**, 328, **335**
Western Regional Research Laboratory, 780, **869**
Weston, C. C., 771, **870**
Wheeler, R. V., 200, **335**, 345, **875**
Whitby, G. S., 64, 66, 69, **75**, 143, **340**
Whitham, H., 685, **870**
Whitmore, W. F., 572, 573, 576, **581**
Whynberg, A., 219
Whyte, D. E., 224, **340**
Wieghard, W., **340**
Wiertalak, J., 761, **870**
Wiesner, J. V., 163
Wilder, E. A., 175, 176, 182, 221, **340**
Wilkin, Robt. E., 408, 409, **442**
William H. Scheel, Inc., 530
Williams, E. F., 43, **74**
Willis, H. B., 772
Willis, J. A. V., 34, 46, **72**
Wilson, G. R., 545, **581**
Wilson, J. M., 859, **870**
Wilson, R. E., 408, 409, **442**
Willstatter, R., 5, **75**
Wimmel, 142
Windaus, A., 598, **635**
Wingfoot Corporation, 523
Winkler, L. W., 585, **635**
Winterstein, A., 279, **340**
Wirth, T., **73**
Wirz, W., **75**
Withers, J. C., 46, **74**
Wittcoff, H., **75**
Wittka, F., 47, 52, **73**
Wolfe, H. J., 835, **870**
Wolper, P. K., 784, **865**
Woltman, A., 470
Wonder Rice Oil Co., 237
Woodward, E. R., 127, **340**
Wool Research Associates, 140
Worden, E. C., **870**
Worgan, G., 775, **870**
Worton, A. G., 820, **870**
Wyman, F. W., 65, 67, **75**
Wynberg, A., 219, **340**

Yamamoto, R., 236, **340**
Yamazaki, R., 43, **75**, 89, 107, 240, **340**, **341**
Yang, P. S., **74**
Yasunga, S., 320, **341**
Young, D. W., **523**, **869**
Yoshikawa, T., 247, **333**

Zaloziecke, R., 357, **376**
Zellner, Julius, 254, 255, **341**
Zentmyer, D. T., 365, **375**, 538, **579**
Zerner, E., **339**
Zetsche, Fritz, 257, 258, **341**
Zhukov, A. A., 46, **75**, 604
Ziegler, M., 361
Zimmermann, A., 213
Ziskin, 769
Zöllner, W., 190, **341**, 360, **376**, 460, **496**, **635**
Zweig, Samuel, 167, 236, 300, 407, **442**
Zopf, L. C., 687, **867**

Subject Index

"Abril Waxes," 525, 541
Absorption creams, 674
Acacia flowers, wax of, *see* Mimosa wax
Acetyl number, 590–595
Acid, abietic, 71, 118, 247
adipic (α,ω-hexanedioic), 52
aleuritic, 60, 113
arachidic (n-eicosanoic), occurrence of, 131, 146, 151, 236, 253, 343
properties of, 34, 35, 38, 44
azelaic (α,ω-nonanedioic), 47, 52
behenic (n-docosanoic), occurrence of, 131, 262, 321, 343
properties of, 34, 35, 38, 44, 629
brassidic, 48, 50
brassylic, (α,ω-tridecanedioic), 52, 53
capric (n-decanoic), 33, 34, 44, 131, 563
carboceric, 366, *see also* Acid carbocerotic
carbocerotic (isoheptacosanoic), 36, 42
carminic, 114
carnaubandioic (docosylmalonic), 54
carnaubic (2?-methyltricosanoic), 31, 35, 41, 169, 171, 206, 242
cerebronic (2-hydroxypentacosanoic) 59, 328
ceromelissic (n-tritriacontanoic), 34, 43, 118
ceroplastic (n-pentatriacontanoic), 34, 43, 118
cerotic, occurrence of, 91, 96, 106, 113, 171, 181, 231
properties of, 34, 36, 38, 42, 84, 91
cetoleic (11-docosenoic), 48, 50, 146
clupanodonic, 45
coccceric (2-hydroxyuntriacontanoic), 59, 114, 264
coccerinic, 114
daturic (15-methylhexadecanoic), 33, 213
decanoic, 34, *see also* Acid, capric
dihydroxy arachidic, 58, 305
— behenic, 59
— dodecanoic (dihydroxylauric), 56, 120
— stearic, 58, 60, 255, 316, 323
docosanedioic (eicosane dicarboxylic) 52, 54, 256, 272
docosanoic, 34, *see also* Acid, behenic
docosenoic, 305
dodecanoic, 34, *see also* Acid, lauric
dotriacontanoic, 34, *see also* Acid, lacceroic
eicosanedioic (phellogenic), 52, 258, 272
eicosenoic, 47, 49, 50, 305
eicosylmalonic, 54
eicosylsuccinic, 54
elaidic, 50, 55
eleostearic, 45
erucic (*cis*-13-docosenoic), 48, 50, 53, 305
ferulic (4-hydroxy-3-methoxycinnamic), 259, 261, 262, 263
ficoceric, 218
gadoleic (9-eicosenoic), 48, 50, 146
gaidic (2-hexadecenoic), 38, 47
geddic, 34, 36, 38, 43, 44, 96, 206
geoceric, 366, 367
gluconic, 6
glutaric (α,ω-pentanedioic), 52
gossypic, 206
hendecylic (n-undecanoic), 33, 34
heneicosanedioic (japanic), 52, 53, 272, 273
hentriacontanoic, 34, 44
heptacosanoic, 42, 168
hexacosadienoic, 46
hexacosanoic, 34, 91, 106, 181, 325, 329, *see also* Acid, cerotic
hexacosenoic, 50, *see also* Acid, ximenic
hexadecenoic, 49
hexatetracontanoic, 34, 38
hexatriacontanoic, 34, 38
hydroxyarachidic, 58, 167
— behenic, 59, 61, 329
— capric, 55, 56, 167
— cerotic, 59, 167, 182, 329
— lauric, 56, 247
— lignoceric, 59, 247, 329
— margaric, 57, 95, 153
— melissic, 59
— myristic, 56, 90, 134

Acid, *Continued*
— octacosanoic (hydroxymontanic), 59, 167
— palmitic, 36, 57, 91, 95, 134, 248
— stearic (hydroxyoctadecanoic) 59, 167, 564, 599, 659
— triacontanoic, 168
hyenic (isopentacosanoic), 35, 42, 89, 368
hypogaeic (*trans*-7-hexadecenoic), 47, 91, 92, 229
ibotaccrotic, 107, 108, 109
ipurolic, 56
isoarachidic, 41, 131
isobehenic, 41, 131, 308, 322
isocapric, 131
isoceroplastic, 43, 265
isocerotic, 42, 131, 366
isogeddic, 43
isohentriacontanoic, 44, 366, 368
isoheptacosanoic (carbocerotic), 42, 168, 169, 326, 366, 368
isolauric, 40, 131
isolignoceric, 35, 41, 131, 326, 328
isomargaric, 40, 213
isomontanic (isooctacosanoic), 42, 131, 366
isomyristic, 33, 40, 131
isononacosanoic, 42, 366, 368
isoplamitic, 40, 131
isopentacosanoic, 40, 366
isostearic, 40, 131
isotricosanoic, 41, 368
jalapinolic (11-hydroxypalmitic), 57
japanic, 52, 54, 272
juniperic (16-hydroxypalmitic), 57, 59, 247, 248
juniperinic (15-hydroxypalmitic), 57
10-ketostearic, 45
13-ketodotriacontanoic, 46, 114
11-ketotriacontanoic, 46
lacceroic, 34, 36, 38, 43, 44
lanoceric (*cis*-dihydroxymelissic), 134
— myristic, 130
— palmic, 51, 133
— palminic, 133
— palmitic, 130
— stearic, 130
lauric (dodecanoic), 33, 34, 39, 44
lauroleic (5 dodecenoic), 49
lignoceric, occurrence of, 35, 92, 131, 259, 261, 262, 343
properties of, 34, 35, 36, 44
linoleic, 44, 45, 48, 259, 298, 312
linolenic, 44, 45, 48, 259
lumequeic (21-triacontenoic), 48, 50
medullic (*n*-heneicosanoic), 34, 38, 168
melissic, occurrence of, 88, 91, 92, 96, 107, 116, 231
properties of, 34, 36, 38, 43
18-methyleicosanoic, 41, 132
24-methylhexacosanoic, 42, 132
20-methyloctacosanoic, 41, 132
28-methyloctacosanoic, 42
10-methyloctadecanoic (tuberculostearic), 40, 51, 325
16-methyloctadecanoic, 41, 132
14-methyltetracosanoic, 35, 42
22-methyltetracosanoic, 42, 132
2-methyltricosanoic, 41, 169
montanic, 34, 36, 38, 44, 92, 231, 366
mycolic, 326, 328
myricinic (*n*-triacontanoic), 34, 36
myristic, 33, 34, 44, 131, 146, 279, 563 *see also* Myristic acid, commercial
myristoleic (cis-9-decenoic), 47
nervonic, 48, 50, 328, 329
nonacosanoic, 34
nonadecanoic, 38, 553, 567
nonadecanedioic, 52, 54
nordihydroguiaretic, 214
octacosanedioic, 52
octacosanoic, 34, 168
octacosylsuccinic, 8
octadecanedioic, 52, 53, 54
octadecylmalonic, 54
oleanolic, 32, 200, 214, 264, 279, 287, 290
oleic (octadecenoic), 47, 49, 88, 259, 305
palmitic, occurrence of, 33, 91, 131, 146, 552
properties of, 33, 34, 38, 44, 563
palmitoleic (*cis*-9-hexadecenoic), 47, 49, 305
pelargonic (*n*-nonanoic), 33, 47, 53, 272
pemphygic, 59, 120
pellonic (22-hydroxybehenic), 59, 256, 258
phloiconolic, 258
phloionic, 258
phthioic, (2,3,21-trimethyltricosanoic), 42, 325
physeteric (5-tetradecenoic) 42, 325

Acid, *Continued*
phytic, 7
pimelic (heptadioic), 52
pisangcerylic, 242
psyllic, 43, 91, 92, 117, 120
ricinoleic, 48, 243
roccelic, 52, 54
rosilic (10-hydroxystearic), 58
rubeabietic, 70, 117, 118
rubenic, 70, 117, 118
sabinic (12-hydroxylauric), 56, 247, 248
sativic, 60, 61, 255
sebacic, 52, 53
selacholeic (*cis*-15-tetracosenoic, 48, 50, 53
shellolic, 54
sorbic, 730
stearic (octadecanoic), occurrence of, 33, 146, 552
properties of, 34, 35, 38, 44, 563
uses of, *see* Stearic acid, commercial
suberic, 52
taricic, 45
tetracosanoic, 34, 106, 236, 326, 329, *see also* Acid, lignoceric
tetracosylmalonic, 8, 54
tetradecenoic, 47, 120
thapsic (hexadefanedioic), 52, 54, 247
triacontanoic, 34, 114
21-triacontenoic (lumequeic), 48, 50, 53
tricosanedioic, 52, 272
trihydroxystearic, 60
tsuzic, 47, 49
tuberculostearic, 40, 51, 325
embellulic (undecyclic), 33
ursolic, 198, 200, 214, 216, 244, 264, 284, 285, 287, 288, 289, 290
vaccenic (*trans*-11-octadecenoic), 47, 50
ximenic, 48, 50
zoömaric, 49, 146
Acid alcohols, polymethylene, 62
Acid amides, 481
Acid anhydrides, fatty, 494
Acid equivalent, definition of, 582
Acid number, *see* Acid value
Acid value, 582, 586–587
Acidolysis, 10
Acids, agno-, 131, *see also* Acids, anteiso monoethanoid
alkyl esters of wax, 65
anteiso monoethanoid, 40–43, 131–133
boiling points of normal chain, 39
commercial waxy, preparation of, 548
densities of solid monoethanoid, 39
dicarboxylic (dibasic), 8, 22, 33, 51–54, 275
dihydroxy, designation of isomers, 55, 60
ethinoic, 45
ethylenic fatty, 46–51
expansion of, 40
fatty, fractional distillation of, 551–553, 555–556
freezing point data of, 38
hydroxy carboxylic, 54–61, *see also* Acid (individual)
hydroxy, designation of position of OH, 9, 55
hydroxy-anteiso, 133
hydroxy-iso, 133
isomers of higher monoethanoid, 8, 36, 40, *see also* Acid, iso-
japanic, 273, 274, 275
keto-carboxylic, 8, 45–46, 114, 169
lano-, 133, 137, 138, *see also* Acids, isomers of higher monoethanoid
melting points of solid keto-carboxylic, 45, 46
methyl-side chain carboxylic, 35, 40, 43
molar volumes of fat and wax, 44
molecular weights of fatty, 44
monoethanoid, 32, 40–43
monoethenoid, 32, 44, *see also* Acids, ethylenic fatty
naphthenic, 541–542
neutralization values of solid fatty, 44
optical isomerism of side-chain, 36, 50–51
paraffin a source of fatty, 553–555, 566–567
polyethenoid, 44
preparation of waxy, commercial, 548
refractive indices of solid fatty, 44
resin (resinolic), 70, 253
role of, in wax formations, 8, 9
sources of commercial fatty, 293, 548, 553, 555
stereoisomerism of monoethenoid, 48–50
unit cell structure of wax, 36

Acid, *Continued*
unsaturated straight-chain fatty, 44, 45, 53
x-ray spacings of solid fatty, 35, 37, 38, 53
Acon wax, 249
"A-C Polyethylene," *see* Polyethylene wax
"Acrawaxes," 487, 494, 858
Acrylic resins, 512
Adeps lanae, 122, *see also* Lanolin
Adhesive, self-sealing wax, 638
Adhesives, use of wax in, 438, 636–640
Adhesive waxed tape, 103, 640
Adipocere wax, 323
Aerosol dispenser, 491
"Aerosol OT," 491, 777, 779
Aerosol spray wax, 491
Afridi wax, 300
Agnosterol, 27
Agricere wax, 323
Aircraft, wax coating materials for, 103, 752, 863
"Albacer Wax," 494
Alcocer wax, *see* Candelilla wax
Alcohol, arachic (*n*-eicosanol), 19, 20, 23, 254, 263, 273
batyl, 148
behenyl (*n*-docosanol), 20, 23
carboceryl, 22, 24, 165
carnaubenyl, 25, 167
carnaubyl, 19, 23, 24, 119, 135, 206, 250, 264, 324
ceroplastyl, 118
ceryl, occurrence of, 23, 88, 89, 95, 103, 106, 108, 109, 115, 118, 243, 265, 266, 289, 307, 315
properties of, 20, 24
cetyl, occurrence of, 3, 23, 144, 147, 153
properties of, 20
uses of, *see Cetyl alcohol*, commercial
chimyl, 148
cyclodecyl (cyclodecanol), 23
decenyl (decenol), 25
docosenyl (docosenol), 25, 305
dodecenyl, 25
docosyl, *see* Alcohol, behenyl
dotriacontanyl (lacceryl), 24
eicosenyl (eicosenol), 25, 305
eicosyl, 20, 148, 324, *see also* Alcohol, arachic
ficoceryl, 268
geddyl (*n*-tetratriacontanol), 20
gossypyl, 206
hendecenyl (hendecenol), 25
heptacosyl, 20, 108
hexacosenyl (hexacosenol), 25
hexacosyl, 233, 288, 367
ibotaceryl, 107, 108, 119
incarnatyl, 21, 24, 102
isobehenyl, 21
isoceryl, 19, 21, 115, 242, 315
isocicosyl, 21
isolacceryl, 21
isolignoceryl, 19, 21
isomontanyl, 21
isomyricyl, 21
isostearyl, 21
koryanyl (isoöctacosanol), 308
lacceryl (*n*-dotriacontanol), 20, 23, 89, 113, 216
lauryl (*n*-dodecanol), 20, 24, 806, 813
lignoceryl, 20, 23, 259, 261, 263, 289
loranthyl, 280
melissyl, 20, 22, 23, 88, 118, 181, 247
montanyl (*n*-octacosanol), 20, 206
myricyl, 20, 23, 24, 89, 172, 192, 279, 307
myristyl, 20, 806
neoceryl, 22, 24, 89, 113, 202
nonadecyl, 20, 280
noneyl (nonenol), 25, 213, 316
octacosyl (*n*-octacosanol), 288
oleyl (octadecenol), 25, 145, 147, 806
palmitoleyl, 25
physeteryl, 25
phthioceryl (phthiocerol), 326
pisangcerylic, 242
psyllostearyl, 22, 24
psyllyl, 102, 120
raphia (isoarachic), 184
selachyl, 148
stearyl (octadecyl), 20, 23, 147, 148, 309, 464, 806
takakibyl, 20, 23
tetracesyl, 20, 24, 367, *see also* Alcohol, lignoceryl
tetradecyl, *see* myristyl
triacontanyl (*n*-triacontanol), 22, 233, 237, 288
zoömaryl, 25
Alcohol waxes, higher, 474
Alcohol, solidified (canned fuel), 663–664

Alcohols, anteiso monoethanoid, 21, 22
commercial production and uses of fatty, 544 *et seq.*
cyclic (cyclonols), 10, 23, 117, 314
determination of, 595
dihydric, 9, 166
dimeric forms of, 22
isomers of normal, 24
ketonic, 10
natural, 18 *et seq.*
natural occurrence of wax, 8, 9, 23
phosphated, commercial, 684
polyhydric, 9, 10, 19
polymethylene acid, 62–63
saturated monohydric, 18 *et seq.*
secondary wax, 9, 23
specific gravities of normal, 25
sulfated, commercial, 684
synthetic, 20
tetrahydric, 251
trihydric, 9
unsaturated monohydric, 10, 25, 26
x-ray spacings of crystals of normal, 8, 19, 24
wax, commercial, 474, 544–545
isomers, 21, 22
"Alcowax," 447, *see also* "A-C Polyethylene,"
Alder bark, wax of, 255
"Aldo Wax," 733
Alfa grass, wax of, 231
Alfalfa wax, 236
Algae peat (dropperite), 346
Algae wax, 343–344
Alkanet root, wax of, 250
Alkyl cyclic ketones, 480, 481
Alkyl esters of wax acids, 65–67
Alkylated polystyrene, 353
Alkanes, 10 *et seq.*, *see also* Hydrocarbons, saturated
Alkenes, 11, 17–18, *see also* Hydrocarbons, unsaturated
"Alpco Wax," 370
Alpha-amyrin (α-amyrenol), 31, 32, 214, 252, 265, 269
Aluminum laminate with paper, 796
— palmitate, 578, 778, 792
— polish, 831
— powder, wax in, 863, 864
— stearates, 573, 574, 578, 864
— tubing, lubricant for cutting, 757
Ambergis, 150–151
"Amberite," 703
American shale, paraffin waxes from, 374
Amide derivatives, aliphatic, 444, 484–485
Amides, long-chain fatty, 481–482
Amine soaps, 531
Ammonium soaps, 531–532, 846
Amyrenols, 29, *see also* Alpha-, and Beta-amyrins
Amyrin esters, 31, 193, 199, 265
Amyrins, 31, 243, 265, *see also* Alpha-, and Beta-amyrins
Analgesic balms, waxes for, 819
Anhydrous wool fat, *see* Lanolin, anhydrous
Aniline point, 165
Animals, waxes from
bird, *Aestrelata lessoni*, 145–146
land, *Ovies aries*, 122
marine, *Balaena rostrata*, 141
Delphinus delephia, 145
Hyperoodon rostratus, 145
Physeter macrocephalus, 141, 145, 146
Ruvettus pretiosus, 149
Animal waxes, classification of, 121
liquid, marine, 121, 146–150
Anolides, 9, 63
Antiblocking agents, 429, 487, 488, 642, 792, 802
Antifoam agent, 543
Antifreeze agents, 542–543
Antimicrobial agents, 730
Antioxidant, for lube oils, 645
for machine parts, 642, 643
for petroleum waxes, 440–441
slushing oils, 643
Antiperspirant cream, 668
Antirust compositions, 642, 643
Antislip agents, 725–726
Antistaling agents, 732
Antistatic agent, 487, 855
Anti-sun checking waxes, 751, 752
Apple skin wax, 23, 288–289
Arachidamide, 482
Arachyl palmitate, 68
Arbol wax, 277
Arbutus leaves, wax alcohols of, 215–216
Arctic sperm oil, 145, 149

Arid plants, formation of wax in, 152–153
"Aristowaxes," 382, 416–417, 714, 715, 847, 859
Arjun wax, 116–117, 118
"Armid Waxes," 482–484, 665, 812
"Armowax," 485–486
Army ration boxes, *see* Ration boxes
Aroclor resin, 804
Artificial fruit, waxing of, 438, 802
Artificial flowers, waxing of, 776, 802
Artificial waxes, *see* Synthetic waxes
"Arwaxes," 510, 804
Asbestos shingles, waxing, 862–863
Attapulgus clay, bleaching with, 408, 427
Automatic sealing, high-speed, 783
Automobile polishes, 823–825
Automobiles, wax spraying, 825
"Avcolube," 855
"Avconit," 856
Axin wax, 114

Baccharis, wax of, 216
Bacillary waxes, 324–328
Bacillus wax, avian tubercle, 326–327
  bovian tubercle, 327–328
  human tubercle, 324–326
Bags, flour, wet waxing, 794
Baking utensils, wax coating, 732
Balanophora wax, 245–246
Balata, 31
Bamboo leaf wax, 242
Banana wax, 242
Banbury mixer, 750
Banding material, tree, 844–845
Barium stearate, 577, 808
Barrel linings, 429, 438
Barrels, pitching of metal, 650
Barks, waxes from, 251
Barrier creams, 676
Batik, 774–775
Battery separators, 459, 699
Bayberry shrubs and wax, 2, 275–277
Bayberry wax, uses of, 279, 654, 768, 845
Bearberry (*Uva ursi*) shrub, wax of, 214
Beard softener, 686
Bee glue, *see* Propolis
Beech bark, wax of, 254
Beeswax, 1, 2, 31, 76 *et seq.*
  binding power with solvents, 713
  bleaching of, 85
  candles of, 655, 662
  chemical composition of, 88 *et seq.*
  coloration of, 77, 82
  crude, 97
  derivatives of, 670
  East Indian, 93
  emulsification of, 533
  figures and models of, 2
  fluorescence of, 415
  hydrophylic derivatives of, 670
  Japanese, 96
  modelling with, 2, 104
  painting with, 656
  recovery of acids from, 92
  refining crude, 80
  rendering of crude, 78
  saponification number of, methods of determining, 81, 82
  solar extraction of, 78
  solvent retention of, 715, 716, 717
  solubility of, 83
  sources of supply of, 79
  substitutes for, 352, 522
  uses of, 103, 664, 668, 674, 690, 807, 835, 849, 854, 863
  vacuum distilled, 498
  white, 81, 87
  world-wide trade in, 87, 98, 102
  yellow, 81, 84–85, 92, 97
Behenin, 313
Behenone, 475, 522
Behenolactone, 61, *see also* Lactones
Behenyl palmitate, 68
Belt dressings, 753
Bending test for waxes, 620–621
Bent grass, wax of, 233
Bentonite, 397, 677, 844
Berry hallocks, waxing of, 743
"Be Square Waxes," 428
Beta amyrin (β-amyrenol), 32, 193, 252, 265, 268, 269
Betulin, 29, 252, 255
Binding power of waxes, with solvent, 713
Birch bark, wax of, 255–256
Bismuth stearate, 575
Bitumens, 342, 649
Bituminization of water organisms, 344
Bituminous pitch, 648–649
Bituminous shales, wax from, 371
Black wax, 436–437, 782
Blasting compositions, wax in, 438, 704

Blasting powders, waxing wraps for, 792
Bleaching clays, 171, 390, 427
Bleaching, of beeswax, 85
of carnauba wax, 171
of hydrocarbons, 389–390, 428
of lignite wax, 373
of microcrystalline waxes, 427
of montan wax, 362–363, 364–365
of ozocerite, 349
of petroleum waxes, 389
Blending of waxes, commercial, 499 *et seq.*
Blocking point test, 615–616
Blood serum, wax of, 329
Blubber oil, 141, 145
"Bohrer's Wax," 491–492
Boiling point, determination of, 625
Boiling points, of alcohols, 20
of alkyl esters, 66
of dicarboxylic acids, 52
of monoethanoid acids, 39
of olefins, 18
of saturated hydrocarbons, 14
Book matches, 767
Book paper, 789
Boot and shoe creams, *see* Shoe polish pastes
Bottle cap lines, 438, 801
Bottle-nose oil, 145, 149
Bottle waxes, 843
Boxes, dip waxed paperboard, 786
Brain material, waxy substances in, 328
Branched-chain hydrocarbons, 13
Brassidine, 477
Brazil wax, *see* Carnauba wax
Bread wrappers, 416, 505, 638, 782–783
Breakfast cereal boxes, 787
Brewing industry, use of wax in, 438, 647 *et seq.*
Bridelia leaf, wax of, 244
Broomcorn, wax of, *see* Sorghum-grain wax,
Broomwax, 210
Bronze powders, wax in, 863
Brown coal, montana wax from, 369
paraffin wax from, 374–375
Brushless shaving cream, 420, 685
Bubble gum, 665, 666
Buchner number (Buchner ratio), 93
Buffing compound, 830
Builders' papers, 398, 792
Building boards, asbestos-cement, 862
Building material, waterproofing, 861
Bumble bee wax, *see* Humble bee wax
Buna S (GRS) synthetic elastomer, 749, 750
Burma crude, wax from, 94
Butchers' wrap, 416, 420
Butea flowers, wax of, 317
Butter, packaging of, 787–788, 798
Butylene polymer wax blend, 802, 803, 804
Butyl methracrylate resin, 754
Butyl rubber, 665, 728, 801

Cable wax, 352, 452, 455, 697
Cacao husks, wax of, 265
Cachalot oil, *see* Sperm oil
Cake mixes, use of wax in, 726, 733
Cakes, wraps for, 782, 790
Calcium naphthenate, 542, 554
— pamitate, 572
— stearate, 569, 572, 577, 578, 579, 715, 760
Camomile flowers, wax of, 321
Candelilla wax, 2, 184 *et seq.*
properties of, 189–191, 194–198, 613, 802
uses of, 196, 665, 679, 695, 703, 754, 772, 821, 848, 849, 857, 859
Candle industry, consumption of wax in, 653
Candleberry wax, *see* Bayberry wax
Candle material, 352, 658
Candle power, unit of, 654
Candles, hardening agent for, 416
shapes and sizes of, 661
spermaceti, 654–655
wax for, 652 *et seq.*
Candle-wick specifications, 661
Candlewood wax, see Ocotillo wax
Candy, chocolate, coating for, 735–736
wax as antistaling agent for, 735
wraps for, 782
Cans, wax lining of, 651
Canvas, treatment of, 397
waxing thread for, 398
Capacitors, waxes for, 457, 698, 699
Capeberry wax, 278
Capric acid, *see also* Acid, capric
Capsules, 438
Carandá (Caranday) wax, 173–175
Carboceryl cerotate, 64

Carbonless transfer paper, 814
Carbon papers, 780, 805 *et seq.*
  waxes used in, 352, 420
Carbonyl group determination, 660
"Carbowaxes," 449–450
  uses of, 449, 665, 678, 688, 750, 814
"Carbowax" stearates, 489–490, 688
Cardboard, wax treated, 538
Carding wax, 777, 779
"Cardis Waxes," 498, 529
Carnauba palm, economic value of, 2
Carnauba wax, 156 *et seq.*
  alcohols from, 24
  blends of paraffine with, 169–170
  chemical composition of, 2, 165 *et seq.*, 587
  consumption of, 173
  flash and fire points of, 164
  grades of, 172
  melting point boosted by, 169–170
  replacements for, 522, 744, 748
  residues of, 172
  solvent extraction and refining of, 161
  uses of, 172, 659, 802, 807, 821, 823, 849, 857, 863
  white, 170–172
Carnaubyl cerotate, 68, 250, 264
  — isobehenate, 68
Carotenoids, 26, 200, 238, 280, 330
Carton liners, waxed glassine, 785
Cartons, waxing of, 503, 504
Cartridge cases, waxing of, 707
Cartridge paper, 704
Carving wax, 779
Casks, waterproofing of, 353
Cassia fistula leaf, wax of, 245
Casting, squeeze mold, 776
Castor oil, fatty acids of, 565
  hardened, 471
Castor oil fish, wax of, 149–150
"Castorwax," 471–473, 638, 660, 777, 791, 801
Catalysts, metallic soaps as, 577
Cauassa leaf wax, 210–211
Cay-cay wax, 280
Ceanothus plant species, waxes of, 198–200
Celery seed, wax of, 308–309
Cellophane, adhesive for laminating, 638
  "MAT," and "MSAT," 731, 796, 803
  moistureproofing, 794–796
  moist wraps for, 731
  "PT," 795
  wax coatings for, 416, 719, 795, 796
Cellulose ether wax, 519–521, 690
Cement bags, 398
Cement, electrical insulating, 487
  hot melt, 639
  waterproofing, 578
Ceramics, wax in, 664 *et seq.*
"Ceramide Wax," 494
Cerasin, Saxon-Thüringian, 355
  Surakhansk, 355–356
Cerates, 144, 815–817
Cereal blades, waxes of, 233
Cereal boxes, *see* Breakfast cereal boxes
Cereal grains, waxes of, 154, 234–236
Cereal wrappers, 787
Cerebrosides, 48, 329
Ceresin, 354
  commercial, 499
  genuine, 354–355
  imitation, *see* Imitation ceresin wax
  lumbricating, 642, 755
  origin of name of, 2, 354
  uses of, 657, 670, 679, 751, 802, 845
Cerin, 257, 258
Cerium stearate, 574, 578
Ceroplastes waxes, 104, 115 *et seq.*
Ceroplastyl melissate, 118
Cerotene, 17, 115, 119
Cerotone, 368, 475
"Certifreash Process," 742
Ceryl aleuritate, 113
  — arachidate, 68, 171
  — behenate, 68, 171
  — carnaubate, 68
  — cerotate, 23, 68, 106, 107, 108, 113, 115, 202, 241, 301, 302
  — hydroxypalmitate, 92, 95, 96
  — lignocerate, 68, 107, 113
  — melissate, 117, 118, 229
  — montanate, 107
  — octacosanate, *see also* Ceryl montanate
  — palmitate, 68, 95, 96, 255, 267, 878
  — stearate, 68, 267, 444
Cetiol, 547
Cetylacetamide wax, 486, 694
Cetyl alcohol, commercial, 3, 23, 144, 546–547

Cetyl alcohol, *Continued*
uses of, 547, 667, 668, 674, 681, 686, 807, 813, 865
Cetyl alcohol ointment, 547, 686, 687, 688
Cetyl esters, 68, 147, 547
— laurate, 68, 147
— myristate, 68, 143, 147
— palmitate, 3, 68, 142, 143, 146, 147, 153
— palmitoleate, 143, 147
— stearate, 68, 143
Cheese, coatings for, 438, 726 *et seq.*
peelable coatings for, 728–729
pouches for, 731
Cherry cuticle wax, 289
Chest rubs, 819
Chewing gum base, 196, 438, 665
Chewing gum wrappers, 785
Chimonanthus flowers, wax of, 321
Chinese candles, 663
Chinese ginkgo tree leaves, wax of, 243
Chinese insect wax, 23, 105 *et seq.*, 113, 838
Chinese tallowtree wax, 310–312
Chlorinated naphthalene, 453–455
— paraffin wax, 450, 639, 645, 646, 647, 696, 856
— rubber (rubber hydrochloride), 515, 809
Chloronaphthalene waxes, 453–455, 696
"Chloropane Wax," 451
Chloroparaffins, 450
Chlorophyll, functions of, 4, 6
Chloroparaffin cyclic condensations, 452–453
"Chlorowax," 451, 452, 455
Chocolate enrobing, 735–736
Cholesterin, 674
Cholesterol, *see* Sterols
Cholesteryl caprate, 28
— esters, 28
— isovalerate, 92
— laurate, 28
— lignocerate, 28
— myristate, 28
— palmitate, 28, 96, 143, 629
— stearate, 28
Chromatographic separations, 181, 214, 257
Citrus fruits, waxing of, 736
Citrus peels, waxes in, 297–300
Cleansing creams, skin, 671–672
Clematis flowers, wax from, 321
"Cleveland Open-cup Tester," 621
Closures for glass containers, wax lined, 800
Cloth, waterproofing, 352, 801
Clover flowers, wax of, 319
Coating waxes, 503–504
Cobalt stearate, 579
Coca leaves, wax of, 213
Coccin and coccid waxes, 104 *et seq.*, 119–120 *see also* Insect wax, of, (classified)
Coccus cacti, wax of, *see* Insect wax (classified)
Cochin-China wax, 280–282
Cochineal wax, 114
Cocoa butter, 265–266, 564, 667, 673, 674, 681, 736, 920
Coconut oil acid, 542
— stearine, 658, 674
Coefficient of expansion of waxes, 433
Coffee berry wax, 312–313
Cold cream, 669
greaseless, 672
Cold-set inks, 840
Collapsible tube, lining, 438
lubricant, 538
Colombian palm wax, 176–177
Colophony, 648, 747, *see also* Acid, abietic
Colophony pitch, 648
Color, determination of, in waxes, 601–602
Colored pencils, *see* Pencils
Colors for waxes, 660, 837, 859–860
Comb foundations, 77
Composition cork, 864
Concrete floors, waxed, 515
Concrete surfacing, 515
Concrete tanks, wax lining, 861
Conifers, waxes of, 246 *et seq.*
Consistency of waxes, determination of, 618–620
Contact waxes, 444, 469
Container board, wet waxing of, 792
Coolers for beverages, waxing, 861
Copper stearate, 572, 577
Copy ink, 805
Coquina tile, 862
Cordage treatment, 544, 578
Cordite, 704

Cork gaskets, 640, 864
Cork inserts, 352
Cork tile wax, 504
Cork wax, 256–258
Corn oil foot wax, 307
Corn wax, 307–308
Cosmetic cream bases, 675
Cosmetic dermatology, 667
Cosmetics, use of wax in, 667 *et seq.*
"Cosmoline," 418
"Coto Flakes," 471
Cotton duck thread, waxing, 398
Cotton wax, 202–207
Coumarone-indene resin, 512, 641, 696, 829
Cowtree wax, 267–268
Cranberry wax, 282–288
Crayons, manufacture of, 398, 688–689
  marking, 690–691
Cream mascaro, 683–684
Cream rouge, 679
Creams, shoe, *see* Shoe polishes
"Crown Waxes," 428–429, 718, 822
Crudes, petroleum, 377
  fractionating, 378–380
Cryoscopic method, 629
Crystal cells, dimensions of, 37
Crystalline substances, identification of, 624
Crystalline types of petroleum waxes, 386
Crystal x-ray spacings, 38, 633
  determination of, 633
Curcus wax, 258
Cyclodecanol, 314, 315
Cycloparaffins, 15–16, 882
Cyclonols, 23, 314, 315

Dairy wax, 502–503
Damar resin, 719, 804, 858
Dandelion root, wax of, 251
Day cream, 675
Decarboxylation in metabolism, 9
Decolorizing agents for wax, 349, 389
"Deenax," 803
Defeathering fowl with wax, 861
Degras, 130, 131, 749
Dehydrated foods, wraps for, 786
Density, determination of, 610
Density change, coefficient of
Dental waxes, 777–779
Dentifrices, 410
Depilatory wax, 678
Dermatitis, 455
Dermoid cists, wax in, 324
Desiccators, wax for, 846
Detackifying agent, wax as, 473
Detonators, wax for, 705
Dewaxing spar varnishes, 111–112
Dialkyl ketones, 475
Dicarboxylic acids, 51–54
  commercial, 275
Dicetyl ether, 547
Dictaphone records, *see* Sound records
Dielectrical measurements, 622–623, 694
Dielectric constants, 696, 700–701, *see also* Appendix
Dielectric strength (KV), 623, 698
Diesters, 587
Diethylene monolaurate, 537
Digitonin test, 28, 596
Diglycol (Diethylene glycol), 537
Diglycol stearate, 537
  uses of, 671, 673, 674, 679, 829, 857
"Diglycol Stearate S," 537, 538
Dihydric alcohols, *see* Alcohols, dehydric
Dihydroxy acids, *see* Acids, dihydroxy
Dika butter, 281, 282
Docosyl behenate, 64, 68
Doegling oil, 149
Dolphin oil, 145
Dopes for carbon papers, 806
Doughnut sugar, wax in, 734
Douglasfir, wax of, 259–263, 714, 717, 847
Drawing crayons, 688–690
Dress forms, 753
Drills, wax for metal, 755
Drinking cups, waxed, 796–798
Dry cell batteries, 172, 352
Drying trays, wax coating, 732
Dry waxing, 792
Duck, wax gland of, 330
"Duo-Sol process," 380
"Durango Wax," 189
"Durez Resins," 499, 530
"Durmont 500 Wax," 498, 499
Durometer hardness, 611–612
  values of waxes, table of, 874–875
"Duroxon Waxes," 492, 534
Dyes for waxes, 660, 680, 839, 859, 860, *see also* Wax-soluble colors

Dynamites, 702
ammonia gelatin, 702

Ear stoppers, 754
Ear wax, 329–330
Earth waxes, 342, 346–348, *see also* Ozocerite
Ecology of plant waxes, 151–152
Egg preservatives, 438
Elaidin, 69
Elastomer-wax mixtures, 512–516
Electrical condensers, wax for, 698
Electrical constants for waxes, 434, 621–622
Electrical insulation, waxes for, 692 *et seq.*
Electric wire, wax coating, 451, 692–693
Electrolytic condensers, 699
Electronic devices, 695
Electroplating waxes, 487
Electrotypers' waxes, 103, 352, 832–833
Embedding compositions, microbiological, 845
Emersol process, 549, 550, 562
Emollients in cosmetics, 668
"Emulsifiable A-C Polyethylenes," 499, 533
Emulsifiable polyethylene waxes, 499
Emulsifiable waxes, natural, 525
synthetic, 499, 525, 526, 533, 534
Emulsifiable wax stocks, 526–527
Emulsification equipment, 527
Emulsifiers, anionic, 524
cationic, 524
Emulsifying agents, 524, 530–533
Emulsions, antifreezing, 542–543
finishing fibers with wax, 543
hydrocarbon-wax, 543
oil-in-water (O/W), 524
processing with wax, equipment for, 738
recipes for wax, for fruit, 737, 738, 739
rust inhibiting wax, 544
scale wax, 528
soap type wax, for polishes, 720
water-in-oil (W/O), 524
Enamelled ware, waxing of, 726
Encaustic, art of, 1
Enfleurage process, 314
Engraver's wax, 833
Enteric coatings, 537, 820–821
Ergosterol, *see* Sterols
"Epolene E," 499, 533
"Epolene N," 448
Erythritol, 10
Esparto wax, 230
uses of, 231, 695, 713, 814, 821, 848
"Estawax," 504
"Ester gum," use of, with waxes, 511
Ester value, 582, 587
Esters, acid, 10
alkyl, table of, 66
cetyl, commercial, 547
estimate of, in waxes, 587
estolidic, 130
ethyl, 64, 65, 66, 476
formation of, in plants, 10, 63
glycol fatty acid, 534, 535
glyceryl fatty acid, 535–537
hydroxystearic, commercial, 565, 659, 660
hydroxylated, 10, 194
methyl, 64, 65, 66, 67
natural wax, 10, 63
polyhydric alcohol fatty acid, 534–535, 537–538
role of, in waxes, 9, 10
simple, 10
unsaturated acid, 147
Estolides, 62, 168, 182, 248
Estrogenic hormone creams, 141, 674, 677
Etholides, 53, 62, 246
Ethyl cellulose, use of, with wax, 520, 772
Ethyl cellulose compositions, 690
Ethylene copolymers, 447
— glycol esters, 535
— interpolymer waxes, 446–447
— oxide polymers, 443
Eucalyptus leaf wax, 244
European elder bark, wax of, 253
Eutectics of fatty acids, 560
Expansion of waxes, 613, 887
Explosives, wax for, 702 *et seq.*
Extreme pressure lubricants, 451
Eyebrow pencils, 683
Eye cosmetics, 683

Fabric, impregnating, 855
wax finishes for, 855
Face powder, 686
Facial make-up, 106, 678

False cyprus leaf wax, 248
Fatty acid amides, 481, *see also* "Armids"
Fatty acid anhydrides, waxes from; 494
Fatty acids, commercial mixed, 555, 556
  determination of total, 583, 590
  distillation of, 551–553
  fractionally distilled, 555–556
Fibers, finishing of, 543–544
Fiber wax, 232, 695, 814
Field ration packages, 438, 800
Figures, wax, 2, 439
Figurines, wax, 352, 416, 846
Finishing wax, shoemakers', 748
Fireretardants, 451
Fireworks, 707
Fischer-Tropsch waxes, 798, 465–466
Fish, wax wraps for frozen, 733
Flake metal powders, 863
Flaking of waxes, machine for, 472
Flameproofing waxes, 452, 455, 494
Flash tests, 621, 827–828
Flatting agent for varnish, 487, 858
"Flavorseal," 740, 742
Flax wax, 201–202, 451
"Flexo Wax C," 494
Floor polishes, 710, *see also* Floor waxes
  rubless, 721–724
Floor waxes, 708 *et seq.*
Floral waxes, crude, 313, *see also* Flowers, waxes of
Florists' paper, 792
Flowers, artificial wax, 352, 802
  modelling, in wax, 775
  waxes from, 313 *et seq.*
Fluorescence of waxes, 415
Foils, laminated metal, 638
Food industry, uses of wax in, 726 *et seq.*
Food packages, termite-proofing, 796
Food ration boxes, 800
Foots oil, slack wax, 394
Forage grasses, waxes of, 233
Formation of waxes by metabolism, 7
Fossil waxes, 342, 343 *et seq.*
Foundation cream, 675
Foundry cores, treating, with wax, 451, 473
Friedelin, 257
Frozen fish, wax wraps for, 733
Frozen foods, packaging of, 514, 732, 786–787
Fruit hairs, waxes from, 249
Fruits, artificial colorings for, 742
  waxes from, 269
  waxing of, 736 *et seq.*
"F-T Waxes," 467, 469, 486, 791, 846
Fungicides, 455, 457, 577, 864
Furfural refining process, 380, 383, 385
Furniture polish, 825
  flash and fire points of, 828
Fur treatment, 543
Furyl ketones, 480
Fuses, 705

Galician mines, 346–347
Galvanized iron wire coating, 439
Garden sage, wax of, 212
Gasket compound, 751
Gedda wax, *see* Ghedda wax
Geddione, 475
Geddyl lacceroate, 68
  — lignocerate, 171
  — melissate, 68, 171
  — montanate, 171
Geneva nomenclature, 19, 55
Gentian root, wax of, 251
German brown coal paraffin wax, 374
German I. G. wax process, 458–460
"Gersthofen Waxes", 443, 461, 462–463, 534, 660
"Gersthofen Wax"
  BJ, 461, 851
  CR, 461, 851
  E, 461, 525, 534
  F, 461, 462, 463
  KPS, 461, 462, 534
  L, 461, 462, 463, 706
  O, 461, 462, 718
  OM, 461, 718
  OP, 172, 462, 711, 712, 715, 718, 851
  S, 461, 462, 706
  Special, 461, 462
  V, 461, 462
Gersthofen processes, 459
Ghedda wax, 83, 93–96
Ghouda cheese, coating for, 727
Glass containers, waxed liners for, 800
Glassines, laminated, 432, 638, 785
  waxed, 351, 432, 783, 786
Glass fabric impregnation, 439
Glassware, etching of, 104
"Glass Wax," 831
Glass wax cleaners, 832

Glues, use of wax in, 640
Glyceria wax, 232
Glycerides, *see* Triglycerides
  mixed, 67, 69, 281, 311
Glyceryl distearate, 536, 537
  ethers, 147, 148
  monolaurate, 536, 537, 684
  monopalmitate, 536
  monostearate, 536, 537, 668, 672, 821, 865, 878
  stearate esters, 536
Glycol (ethylene glycol), 534
  dilaurate, 534
  dipalmitate, 535
  distearate, 534, 536, 537
  monolaurate, 537
  monopalmitate, 534, 535
  monostearate, 534, 535, 537, 635
  "Stearate S," 538
  waxes, 525
Glycols, 534
Glycostearin, 537, 673
"Glycowax," 494
Golden weed, wax of, 216
Gondang wax, 268
Grafting wax, 844
Gramaphone records, *see* Sound records
Grammer spraying machine, 755, 780, 793
Grapefruit peel wax, 298–300
Grape pomace wax, 290
Graphite pencils, 691
Grasses, waxes of reed, 230
Greaseless cold cream, 672
Greaseless ointments, 672
Grease, lubricating, 473, 578, 644, 756
Greaseproof coatings, 495
Greaseproof paper, 784, 789
Green lint cotton wax, 204
Guayule, wax of, 269
Gueriniella wax, 295
Gunpowder, wax wrap for, 702
Gun wads, use of wax in, 640
Gutta percha (gum gutta), 665, 779

Haftax Wax," 525
Hair dressing, 678
Hair pomade, 677
Hair straightener, 577
Halogenated naphthalene, 453, 454, *see also* "Halowax," and "Nibrenwax"
"Halowaxes," 452, 456–457, 813
Handcleaners, waterless, 678
Hardness values of waxes, 83
Hartshorne bleaching process, 390
Heat and sound insulation, 863
Heat of fusion of waxes, 411, 413
Heat-sealing compounds, 438
Heat-sealing foils, 780
Heat-sealing wax papers, 782, 786
Hechner number, 583
Hemp wax, 207–208
Henequen (hemp) wax, 208–209
Hexacosyl stearate, 64, *see also* Ceryl stearate
Hezel method of saponification, 82, 190, 586, 894
Hoarhound leaves, wax of, 215
Honeycomb foundation, 77, 103
Hormone cosmetic preparations, 141, 674
Horticultural binding tape, 642
Horticultural wax, 438
"Hot melts," 784
Hot melt cements, 487, 639, 784
Hot coatings, 639, 785
Household wax, 409, 860
  waxed paper, 780, 782
Hübl number, 600
Human blood serum, wax of, 329
Humble bee wax, 102
Humus formations, 346
Hydrocarbons, bleaching by clay, 389, 390
  boiling points of, 14
  branch-chain paraffin, 13
  crystal types of, 13, 16
  cyclic, 15
  densities of, 11, 12, 18
  determination of, in waxes, 595
  formation of, in nature, 9, 10, 11
  heats of fusion of, 413
  individual liquid, cetene, 18
    heptadecene, 16, 18
  individual solid, cerane (isohexacosane), 13
    cerotene, 17, 18, 115
    cetane, 419
    cholestane, 30
    1-cyclohexyleicosane, 16
    1-cyclopentylheneicosane, 16
    docosane, 12
    docosylene (1-docosene), 18

Hydrocarbons, *Continued*
dotriacontane, 12, 13, 207, 405, 419
dotriacontene, 17, 18, 207
eicosane, 12
eicosylene (eicosene), 18
heneicosylene (heneicosene), 18
hentriacontane, 12, 15, 92, 95, 155, 171, 181, 192, 207, 343
hentriacontene, 18
heptacosane, 12, 92, 95, 96, 106, 169, 171, 244
heptocosylene, 17, 18
heptadecane, 12, 404, 419
hexacosane, 12, 13
hexacosylene (hexacosene), 18
hexadecane, 12, 419
isohexacosane, 13
isoöctacosane, 13
isotetracosane, 13
isotriacontane, 15
melene (1-triacontene), 18, 92, 96
melissane (isotriacontane), 14
nonacosane, 12, 92, 96, 171, 194, 202, 244, 284, 320
nonacosylene (nonacosene), 18
octacosane, 12
octacosylene (octacosene), 18
octadecane, 12, 419
octadecylene (octadecene), 16, 18, 419
pentacosane, 12, 92, 320
pentadecane, 12, 153
pentatriacontane, 12, 265, 345
phthiocerane, 15
squalene, 16, 241
tetracontane, 12, 15
tetracosane, 12, 406
tetracosylene, 18
tetratriacontadiene, 430
tetratriacontane, 12, 264, 430
triacontane, 12, 15, 207, 320
tritetracontane, 12
tritriacontane, 12, 192, 194
lignite fossil, 345
melting points, vs mol. weights of, 389
specific gravities of, 388
naphthenic, 377
petroleum, classification of, 377
role of, in waxes, 9, 11, 344
saturated wax, 10–11
crystal types of, 16
physical properties of, 11–16
unsaturated wax, 16–18
viscosity in poises of, 13, 389
wax emulsions of, 543
x-ray pattern of, 13
Hydrocarbon waxes, synthetic, 465 *et seq.*
Hydrogenated castor oil, 444, 471
— castor oil wax, 471, 472
— corn oil, 471
— cottonseed oil, 444, 470, 471, 792
— jojoba oil, 303, 306
— marine oils, 470, 471, 473
— rice oil, 241
— rice wax, 241, 242
— soybean oil, 471
— sperm oil, 474, 732
Hydrogenation of oils, 470 *et seq.*
Hydroxy acids, 54
table of, 56
Hydroxystearic acid, commercial, 564, 644, 657, 659, 660
Hydroxyl number, determination of, 590
12-Hydroxystearic acid, commercial, 756
12-Hydroxystearin, 472
Histological mounting wax, 845

Ice cream, waxed cartons for, 798
Identifications of crystalline substances, 624
"I. G. Waxes," 457 *et seq.*, *see also* "Gersthofen Waxes,"
Imitation ceresin wax, 172, 355, 499–500
Imide condensation derivatives, 487
Indian corn, wax of, 307
Indian sorrel, wax of, 212
Indices of refraction, *see* Refractive indices
Indigo plant, wax of, 212
Inks, *see* Printing inks
Inlay-casting wax, 778
Inositol, 7, 10
Insect host plants for wax production
Croton lacciferus, 109
Fagus sp., 115
Fraxinus chinensis, 105
Helianthus bolanderi, 77
Ligustrum luditum, 105
— *ovalifolium*, 108
Lonicera xylosteum, 120

Insect host plants for wax protection, *Continued*
Mimosa acutifolia, 116
Nopalea cochenillifer, 114
Opuntia ficus indica, 114
— *tuna*, 114
Papaver californicum, 77
Taraxacum officinale, 77
Terminella arjuna, 116
Trifoleum repens, 78
Insecticide spray emulsions, 864
Insect wax
Apis adansonii, 77, 98, 99
— *caffra*, 77
— *dorsata*, 76, 77, 93, 94, 98
— *facista*, 77, 93, 98
— *florea*, 76, 77, 93, 94, 98
— *indica*, 76, 77, 93, 94, 98, 99
— *mellifera*, 76
— *mellifica*, 76, 93, 94, 97, 98, 99
— *peroni*, 93, 99
— *scutelata*, 77, 99
— *sinensis*, 93
— *unicolor*, 77, 99
Bombus lapidarius, 102
— *terrestris*, 102
Bombyx mori, 121
Brahamea japonica, 106
— spp. (species), 104
Carteria lacca, 104, 109
Cerococcus muratae, 115
Ceroplastes ceriferus, 116, 117
— *destructor*, 116, 119
— *floridensis*, 116, 117
— *grandis*, 116, 119
— *rubens*, 116, 117, 118
Coccus axin, 114
— *cacti*, 104, 113
— *ceriferus*, 104, 105, 106
— *pela*, 104, 105
Cryptococcus fagi, 115
Dactylopius opuntiae, 114
Ericerus pela, 105, 107, 108
Erytherus pela, 108
Galleria mellonella, 121
Iceria purchasi, 119, 121
Melanoplus differentialis, 121
Melipona laeviceps, 101
Pemphygus xylostei, 120
Prontapsis yanonensis, 120
Pseudococcus cacti, 114
— *citri*, 121
Psylla alni, 120
— *buxi*, 120
Pulvinaria horii, 114
Saskiaspis pentagona, 119
Tachardia lacca, 104, 109, 113
Tachardina theae, 119, 120
Insects, waxes from, 76
Insectproofing of waxed paper, 796
Insect repellent cream, 865
Insulating braid, electrical, 416
Insulation and wall boards, wet waxing of, 794
Insulation waxes, electrical, ratings for, 700
Intaglio printing inks, 837
Interplanar x-ray spacings, 13, 37, 38
Investment casting, 771
Iodine number, determination of, 588–589
Isoceryl carnaubate, 242
— isocerotate, 241
Isomers of wax acids, 40, 41, 42, 43
Isoparaffins, 355, 375, 419

"JAA Wax," 198
Jambul fruit, wax of, 296
Japanwax, 270 *et seq.*
uses of, 273, 273, 666, 762, 792, 847, 854
Japanese insect waxes, 96, 99, 116
Jar closures, liners for, 800
Java kapok lint, wax of, 249
Java wax, *see* Gondang wax
Jelly glasses, 409, 860
Jojoba wax (jojoba oil), 302 *et seq.*
hydrogenated, 303, 306, 819
Journal grease, 562, 756
Juniper trees, waxes of, 246

Kamala, wax of, 249
Kaoling grains, wax from testa of, 236
Kapok lint, wax of Java, 249
"Karawax," 525, 526
Kegs, waxing wooden, 429
Ketones, alkyl cyclic, 480
determination of, 600
hydroxy, 480
uses for dialkyl, 479
waxlike, 475 *et seq.*

Keto-acids, table of, 45
Ketonic alcohols, 10
Kinematic viscosity, 618, 874
Kohlrabi, wax of, 212
Koryan corn oil, 23
Kraft paper, waterproofing, 397
Kropscott process, 521

Label papers, 792
Labels, wax adhesive for, 641
Label varnish, 858
Laccerone, 475
Lacceryl cerotate, 68, 171
— lacceroate, 68, 113
— palmitate, 68
— triacontanate, 68
Lacquer, wax in, 795
Lacryma wax, 233
Lactone number, determination of, 599-600
Lactones, delta (δ), 61-62, 92, 599
gamma (γ), 61, 62
omega (ω), 62, 92, 171
Lac wax, 111, 522
Laminating adhesive, wax as, 352, 438, 637, 781
Laminated glassines, 785
Laminated wrapping material, 352, 796
"Lanette Wax," 525, 526, 678, 686, 864
Lanolin, 121, 127 *et seq.*
anhydrous, uses of, 642, 673, 674, 677
hydrous, uses of, 674, 678, 744
Lanolin, absorption base, 675, 681
acids, commercial, 140
concentrates, 128
derivatives, 138
Lanosterol, *see* Pseudosterols
Larrea leaves, wax of, 214
Latex rubbers, uses of wax in, 752
Latex products, lubrication of, 750
Latex trees, waxes from, 267
Launching lubricants, 759
Laundry wax, 144
Lauric acid, 563, *see also* Acid, lauric
Laurone, 444, 476, 477, 479, 713, 878
Lead pencil carbons, 811
Lead pencils, *see* Pencils
Lead stearate, 576, 578
Leaf blades, waxes of, 233
Leaf casting in wax, 776
Leather dressings, 196, 746
Leather finishing, 747, 748
Leather industry, use of wax in, 744 *et seq.*
Leather polishes, 747
Leather preservatives, 744, 745
Leather seasonings, 744, 745
Lecithin, 673, 674, 736
Licuri wax, 179, *see also* Ouricury wax
Liebermann-Burchard reaction, 597-598
Lignin structure of, 5
Lignite, fossil waxes, 345
montana wax, 360 *et seq.*
paraffines, 342, 371 *et seq.*
process of extraction, 361
tar distillate, 363
Lignite wax, 343
Alexandrian, 363
Devonshire, 370
South Indian, 371
uses of, 527
Lignocerin, 313 *see also* Triglycerides
Lignoceryl palmitate, 68
Linens, lustering of, 144
Linolin, 70, 313
Linolenin, 70
Linoleum, wax for, 492, 857
Linseed oil, wax of, 301
"Lipettes," 683
Lip rouge, liquid, 679
Lipstick, 679 *et seq.*
Liptobioliths, 345, 346
Liptobiolithic waxes, 345, 356
Liquid cream shampoos, 684
Liquid floor polishes, 719 *et seq.*
Liquid paraffin, *see* White mineral oil
Liquid petrolatum, 420
Liquid stove polish, 829
Liquid waxes, definition of, 144
Lithium hydroxystearate greases, 473
— stearate, 571, 577
Lithographic prints, waxing of, 755, 780, 793
Locker paper, 733, 781
"Lorol," (lauryl alcohol, commercial), 24
Lost wax art process, 770
Lotions, wax in, 538
Lube oil raffinates, dewaxing, 421
Lubricant, stick-type wax, 755
Lubricating grease, 644, 756, *see also* Greases

Lubricator, wax as, 754 *et seq.*
Lucerne leaf (alfalfa), wax of, 236
Lumber, wax treatment of, 760
Luminescent paint, 578
Lupeol, 29, 31, 243, 252, 265, 269, 320
Luster cleaners, 395
Lustrous finishes, 792

Machine parts, rustproofing, 642
Machine tools, wax lubricating, 755, 757
"Machine wax," 747
Madagascar waxes, 184, 216–217
Magnesium stearate, 570, 571
Malol, *see also* Acid, ursolic
Manila resin, 638
Manley process of dewaxing, 383
Manzanita leaves, wax of, 200
Maquenne melting-point block, 604
Marine algal wax, 343
Marine animal waxes, classification of, 121
Marine fossil waxes, 343 *et seq.*
Marine oils, 473–474
Marine plant waxes, 344
Marking crayons, 690
Mascara, *see* Eye cosmetics
Masking tape, 641
Mass spectrometer analysis, 630 *et seq.*
Master carbon sheet for transfer, 812
Matches, 761 *et seq.*
  book, 767
  Italian safety, 766–767
  Swedish, 765
  wax, *see* Wax matches
Match wax, 755, 764
Matrix for printing, 769
Meat coatings, 438
Meat wrapping paper, 787
Mechanical packings, 812
Mechanical rubbers, 552, 752
Meerschaum pipes, wax costing, 846
"Mekon Waxes," 429
Melene, 17, 18
Meliponen wax, *see* Trigona wax
Melissone, 475
Melissyl alcohol, *see* Alcohol, melissyl
  — carbocerotate, 68, 108
  — melissate, 68
Melting point, depression of, 15, 37
  elevation of, 169–170, 178, 232
  methods of determining, 602 *et seq.*
Melting points, of dicarboxylic acids, 52
  of esters, lower alkyl, 66, 67
  of esters, natural wax, 68
  of hydrocarbons, 12
  of hydroxylated monoethanoid acids, 56 *et seq.*
  of iso monoethanoid acids, 41 *et seq.*
  of keto carboxylic acids, 45–46
  of monoethanoid alcohols, 20–22
  of monoethenoid acids, 49, 50
  of normal ethanoid acids, 34
  of petroleum waxes, 608–609
  of waxes, tables of,
Metabolism of plants, 22
Metal cutting, 451
Metal drilling lubricants, 754, 755, 757
Metal drum lining, 429
Metal finishes, 544
Metal foil, coating, 512
  laminated, 638
Metal polish, 831
Metal powders, wax in flake, 865
Metal stamping, wax for, 562,
Metallic soaps, 568 *et seq.*
Metallurgy, use of wax in powder, 771
Metals, oxidation effects of, on waxes, 440
Methyl behenate, 66, 67
  — esters, 64 *et seq.*
  — -glyoxal, 4
  — hydroxystearate, commercial, 463
  — montanate, 64, 66, 67
  — stearate, 64, 66, 67
"Micris Wax," 429
Microcast process, 771
Microcrystalline wax, adhesive types, 437
  blends of, with paraffine, 437
  brands of, 428
  cloud points of, 435
  determination of oil content in, 437
  electrical properties of, 434
  lube oil raffinates as source of, 421
  oxidized, 520
  penetration indices of, 433
  physical constants of, 430 *et seq.*
  recovery of, 424, 426
  refining of, 427, 428

Microcrystalline wax, *Continued*
solubility of, 434
uses of, 429, 432, 438, 665, 667, 751, 863
Microörganisms, action of, on hydrocarbons, 701
Microscopic slide mounts, 462
"Micro Wax," 421, 436
Mildewproofing, 438, 542
Milk bottles, waxed paper, 798 *et seq.*
Milkweed, wax of, 269
Minera waxes, 3, 353
Mistletoe berry wax, 279
Modelling flowers in wax, 104, 775
Modulus of rupture test, 882
Moistureproofing cellophane, 794
Molar refractivity, 634
Molar volume, 44
Mold-release agents, 538, 577
Molding and casting techniques, 767 *et seq.*
Molding material, 768
Mold fungus inhibition, role of wax in, 577, 864
Mold lubricant, 473
Moldproofing agents, 451, 864
Molecular distillation, 626
Molecular weight determinations, 627
Mona wax, 356, 359
Monoethanolamine stearate, 531
Monoglycerides, 536
Monolaurin, 536, 537
Monomyristin, 564
Monostearin, 536
Montana waxes, 342, 343, *see also* Montan wax
Montan glycolate emulsifier, 538
Montanic acid, commercial, 568
Montanic ester wax, 461, 863
Montanilla wax, 365
Montanin wax, 356, 359
Montanone, 475, 477, 568
Montan wax, 356, 360 *et seq.*
American, 356, 369-370, 748, 807
crude, 360, 361, 834, 848
Czechoslovakian, 356, 368-369
deresinified, 360
Devon, 356, 370-371
double refined, 367, 848
fully bleached, 364-365
Polish, 369
Riebeck, 356, 360 *et seq.*, 370
sulfonic acids of, 368
uses of, 367, 368, 659, 744, 748, 807, 848
Montanyl cerotate, 68
— lignocerate, 68, 107, 171
— montanate, 68
Mop oil, 709
"Morax," 506, 508
Morpholine soaps, 531
Motor oil waxes, 382
Motor parts, waxing, 352, 643
Motta test, 181
Moulage, 768–769
Mudar bark wax, 264–265
Multiple copy transfer paper, 812
Mummies, use of wax in, 1
Munitions, *see* Explosives
Murmurú wax, 294
Mutton bird oil, 145
Mycosterols, 26
Myrica waxes, 275 *et seq.*
Myricin, 89
Myricyl cerotate, 68, 92, 181, 182, 241
— hypogaeate, 92
— hydroxypalmitate, 96
— isobehenate, 68
— lacceroate, 118
— lignocerate, 68, 171
— melissate, 243, 321
— montanate, 68
— palmitate, 68, 89, 92, 96, 202, 237
— stearate, 68
— triacontanate, 68, 295
Myristic acid, commercial, 293, 562, 563, 564
Myristica tallows, 291 *et seq.*
Myristin, *see* Trimyristin
Myristyl caprate, 147
— myristate, 68, 143

Nail polish remover, 678
"Napalm," 542
Naphthalene-sulfonic acid, ethers of, 533
Naphthenates, 542
Naphthenes, 375, 541, 542
Naphthenic acids, 541–542
— hydrocarbons, 377
"Neo-Fats," 479, 562
Neoprene, 752
Neutralization equivalent, 582
Neutralization number, definition of, 582
Neutralization values of acids, 44

"Neville Resin,"
"Nibren Wax," 455
Night cream, 673
Nigrosine, 809, 813, 829, 852
Nitrocellulose lacquer, wax in, 795
Nitrocellulose powder, wax in, 703
Nitro waxes, 702
Nonabrasive body polish, *see* Polishes
Nonfibrous wrappings, moistureproofing, 794
Nonsaponifiable matter, det'n of, 583
Nourishing cream (absorption cream), 674
Nutmeg butter, 291, 292, 293

Ocotillo wax, 263
Octadecamide, *see* Stearamide
Octadecyl 12-hydroxystearate, 462
— palmitate, 68
— stearate, 68
Ocuba wax, *see* Ucuhuba wax
Oil, arctic sperm, 146 *et seq.*
bottlenose, 149
doegling, 149
jojoba, *see* Jojoba wax
whale, 150
Oil content in paraffine, 407
Oil-soluble colors, 859
Oil-uptake by waxes, 712
Ointments, 817, 819
Okonite, 349
Oleander bark, wax of, 264
Oleanol, 255
Oleanolic acid acetate, 200
Olefins, wax, 16–18
Olein, 147
Oleodipalmitin, 311, 663
Oleomyristopalmitin, 311
Oleone, 477, 480
Oleyl alcohol, 147
— myristate, 147
— oleate, 147
Olive bark, wax of, 265
OMC waxes, 529–531, 807, 822
"Opalwax," 472, 473, 713
Opium wax, 295
"Oppanol," 802
Optical isomerism, 50
"OP Wax," see "Gersthofen Waxes"
Orange leaves, wax of, 213
Orange peel, wax of, 297, 298
Ordnance packing, 438
wrappings, 702, 703, 704, 707, 796
Organogenic rock formations, 346, 347
Ornament coating wax, 846
Ouricury wax, 178 *et seq.*
economic value of, 182–183
uses of, 182, 713, 744, 772, 821, 822, 835, 863
Ouropaido wax, 179
Oxidized hydrocarbon waxes, 498, 528, 644, 807
Oxidized micro (OMC) waxes, 498, 529–530, 724
Oxo molecular waxes, 493, 660
Oxo synthesis of wax alcohols, 545–546
Ozocerite, 342, 346, 348 *et seq.*
American, *see* American mineral wax
artificial, 353
chemical composition of, 351
Galican, 348, 350, 354
mining of, 346–347
refining of, 347, 348–349
uses of, 351–352, 668, 679, 751, 833, 838, 851
Utah, 347, 353–354
Ozokerite, American petroleum, 353, *see also* Petroleum ceresin
uses of, 785

Packings, steam, 352
Pails, waterproofing, 353
Paint, wax in, 397, 487, 494, 578, 858
Paint remover, wax in, 196, 858–859
Palmitamide, 482
Palmitic acid, commercial, 311, 563, 564
Palmitin, 70, 313, *see also* Tripalmitin
Palmitolactone, 61
Palmitodiolein, 311
Palmitone, 245, 444, 476, 477, 479, 660, 713
hydroxy, 245, 477
Palmityl alcohol, *see* Cetyl alcohol
Palm tree waxes, 154 *et seq.*
Palm wax, Colombian, 176–177
commercial, 177–178, 859
Paper drinking cups, waxed, 780, 796–798
Paper, applying wax to, 780–781
beater, wax for, 527, 729
-board containers, 781, 792, 798
bread wrappers, *see* Bread wrappers
lubrication of, 538

Paper, *Continued*
milk cartons, 798 *et seq.*
packaging, protective, 781–782
paraffined, 783
products, wax application to, 779 *et seq.*
refrigerator locker, 753
wax laminated, 784
waxed, 782 *et seq.*, 786, 790
waxes used for, 791–792
waxing of, 780, 792 *et seq.*
Paper sizings, wax in, 788–790
Paraffin wax, 393 *et seq.*
acids from, 553
American refined, grades of, 403
from American shale, 374
Asiatic refined, 404
block, 398
-carnauba wax blends, 170
chlorinated, 450
composition of, 394, 882
consumption of, in paper industry, 780
crystal habit of, 405–406
crystalline types of, 386, 407
definition of term, 401
density of, 409–410
distillate, pressable, 393–394
durometer hardness of, 402
fluorescence of, 415
fully refined, 401–403
German brown coal, 374–375
grades of, 403
heat of fusion of, 411
influence of air on density of, 411
lignite, *see* Lignite paraffine
microbiological failures with, 701
molecular weight of components of, 410
oil content, determination of, in, 407
origin of name, 401
packaging of, 417
palletizing of, 417
penetration values of, 414
physical tests for, 402
range of hydrocarbons in, 404–405
recovery of, from petroleum, 393 *et seq.*
refractive index of, 408
residual oil content in, 409
Scottish shale oil, 373
slop, 378
softening point of, 413
solubility of, in solvents, 412, 413
sources of, 377, 379, 393
specific heat of, 411
standards for, 403, 409 *et seq.*
synthetic, 444, 463
tank car handling of, 417, 790
thermal conductivity of, 411
uses of, 653, 658, 668, 703, 744, 749, 751, 765, 791, 863
USP, 402
"Parowax," 409, 769
Parcel wax, 840
Parchment, waxed vegetable, 786
Parlor matches, 766
"Parmos" (petrolatums), 420
Pastels, 689, *see also* Crayons
Paste type polishes, *see* Polishes
Patternmaker's wax, 104
Pear cuticle wax, 289
Peat wax, 356 *et seq.*
Pe-la wax, 105
Pelletized fuel, use of wax in, 864
Pencils, colored, 691
copying, 691
graphite, 274, 691
Penetration test, 414, 612–613
Penetration indeces of waxes, 414, 433
Penicillin injection in oil and wax, 818
"Pennsylvania Micro Wax," 436
Pentaerythritol esters, 538
"Pentowaxes," 538
Perfume fixative 547
Peroxide cream, 675
Peroxide method of bleaching lipide waxes, 85
Perubalsam balm, wax of, 296–297
Petrolatum, 417–420
liquid, 420, *see also* White oil
technical, 417–418, 823
uses of, 419, 420, 642, 643, 790, 792, 809
Petrolatum stock, 424
Petrolatum wax, 421, 423, 781
Petroloum, crude, 377–378
formation of, 344
processes of refining, 378 *et seq.*
sources of, 377–378
Petroleum ceresin waxes, 354, 421, 675, 796, 823, 854
Petroleum jelly, 418, *see also* Petrolatum
Petroleum raffinates, selective solvents for, 422
Petroleum sulfonic acid, 532
Petroleum sulfonates, 526, 527, 532, 644

Petroleum waxes, 377 *et seq.*
bleaching of, 389–390
classification of, 391–393
crystal types of, 386
preventing oxidation of melts of, 439–441
sources of, 377–378
"Petronauba Wax," 530
"Petrosene Wax," 432, 433, 440
"Petrowax," 637, 769
Pharmaceuticals, use of wax in, 815 *et seq.*
Phlegmatizing wax, 706
Phonographic records, *see* Sound records
Phospholipides, 241
Photographic films, wax in, 172
Phthalimides, 488
Physical constants, determination of, 601 *et seq.*
tables of, 871 *et seq.*
Phytosterols, 26, *see also* Sterols, individual
Phytin, 7
Phytoplankton, wax of, *see* Algae wax
Phtol, 6
Phytosterolin, 321
Phytosteryl palmitate, 202, 308
Phytosterols, 26, 214, 258, 266, 597, *see also* Sterols
Pickles, waxing, 731
Pill coatings, wax for, 820, *see also* Enteric coatings
Pineapple cuticle, wax of, 289
Pine chermes, wax of, 247
Pipe coatings, wax type, 861
Pipe still process, 379
Pisang wax, 242
Pituri shrub, wax of, 244
Plant lice, wax constituents of, 120
Plant metabolism, 4 *et seq.*
Plant metamorphosis, 4, 51
Plants, waxes from
Abies alba, 247
— *picea*, 247
Acacia cavenia, 317
— *constricta*, 317
dealbata, 317
— *farnesiana*, 316
— *greggi*, 317
— *vernicosa*, 317
Acer pseudoplatanus, 266
— *rubrum*, 152
Adenostoma fasciculatum, 322
Agave fourcroydes, 154, 207, 208
— *rigida*, 208
— *sisalana*, 154, 208, 209, 345
Agrostis alba, 233
Ailanthus altissima, 266
Alchemilla alpina, 14
Alkanna tinctoria, 250
Allium sp. (species), 151
Alnus viridis, 255
Alstonia scholaris, 252, 265
— *venenata*, 31
Ananas comosus, 280
Andromeda polifolia, 152
Andropogon sorghum, 234, *see also Sorghum sp.*
Anthemus nobilis, 321
Apium graveolens, 308
Aplopappus laricifolius, 216
— *tenuisectus*, 216
Apocynum andrososaemifolium, 251
Arbutus unedo, 215
Arctostaphylos glauca, 200
— *uva-ursi*, 287
Arisaema triphyllum, 28, 206
Artimisia vulgaris, 276c
Asclepias linaria, 269
— *syriaca*, 269
Astrocaryum murumuru, 155, 294
Attalea excelsa, 154, 178, 179
— *funifera*, 155, 178
Baccharis sarothrides, 216
Balanophora elongata, 245
— sp., 154, 246
Betula lenta, 31, 252, 255
— *verrucosa* (*B. pendula*), 255
Biota orientalis (*Thuja orientalis*), 248
Borassus flabellifera, 155
Brassica oleracea botrytis, 151
— — *gemmifera*, 23
— — *italica*, 212
Bridelia stipularis, 244
Brosium alicastrum, 267
— *galactodendron*, 267
Bulnesia retama, 196, 197
Bucerus catappa, 265
Butea frondosa, 317
— *monosperma*, 317
Buxus chinensis, 302
Calamus rotang, 155
Calathea lutea, 154, 210

Plants, *Continued*
Calendula officinalis, 279
Calotropis gigantea, 252, 264, 265
Camellia japonica, 212
— *sasanqua*, 212
— *sinensis*, 212
Cannabis sativa, 207, 208
Capparis spinosa, 152
Carex arenaria, 233
— *panicea*, 152
Carpinus betulus, 255
Carthamus oxycantha, 300
— *tinctorius*, 300
Cassia fistula, 245
Ceanothus crassifolius, 198, 199
— *oliganthus*, 198, 199, 200
— *velutinus*, 154, 198
Cedrus sp., 246
Ceiba pentandra, 249
Ceratonia siliqua, 266
Cerozylon andicola, 154, 176
— *ceriferum*, 176
— *ferrugineum*, 156, 176
— *quindiuense*, 156, 176
Chamarcyparis obtusa, 248
— *pisifera*, 248
Chimonanthus fragrans, 321
— *praecox*, 321
Cichorium endivia, 267
— *intybus*, 267
Citrus aurantium, 213, 297, 298
— *aurantifolia*, 297
— *bergamia*, 297
— *grandis*, 299, 320
— *indica*, 297
— *limetta*, 297
— *limonia*, 297
— *maxima*, 320
— *nobilis*, 297
— *paradisi*, 297
— *sinensis*, 297
— *vulgaris*, 297, 298
Clematis vitalba, 321
Clusia flava, 267
— *venezuelensis*, 267
Cocos coronata, 155, 177, 178, 179, 181
Coffea arabica, 312
Coix lacrymajobi, 151, 155, 233
Convallaria majalis, 319
Copernicia australis, 155, 173
— *cerifera*, 154, 156, 174
Corchorus capsularis, 207
Cornus sanguinea, 255
Corypha cerifera, 173, 174
Covillea tridentata, 152
Crambe maritima, 152
Crataegus oxycanthus, 266
Crotalaria juncea, 207
Cynanchum messeri, 216, 217
Cyperus papyrus, 233
Cytisus junceus, 210, 319
— *scoparius*, 210
Dacrydium cupressinum, 200
Dactylis glomerata, 155, 233
Datura stramonium, 33
Dianthus caryophyllus, 151
Duboisia hopwoodi, 244
Elaëis guineënsis, 155
Elymus arenarius, 152
Eriodendron anfractuosum, 144, 249
Eriophorum vaginatum, 233, 358
Eryngium, aritinum, 152
Erythroxylon coca, 213
— *novogranatense*, 213
— *truxillensis*, 213
Eucalyptus aceryula, 244
— *globulus*, 151, 155, 244
— *oleosa*, 244
— *paladusa*, 244
— *smithi*, 244
Eugenia jambolana, 296
Euonymus europaeus, 266
Euphorbia antisyphilitica, 154, 184, 185, 186, 189, 190, 191
— *balsamifera*, 31
— *cerifera*, 185, 189, 191
— *pilulifera*, 184
— *resinifera*, 184, 217
— *stenoclada*, 154, 184, 216, 217
— *xylophylloides*, 154, 216, 217
Exogonium purga, 250
Fagopyrum, sp., 233
Fagus sylvatica, 252, 254
Ficus alba, 268, 269
— *ceriflua*, 268
— *elastica*, 268
— *elastica variegata*, 268
— *fulva*, 269
Filipendula ulmaria, 310
Fouquieria splendens, 154, 207, 252, 263
Fucus vesiculosus, 344
Furcraea gigantea, 154, 207
Galacdendron utile, 267

Plants, *Continued*
Gentiana lutea, 251
Ginkgo biloba, 243
Glaucium flavum, 152
Globularia alypum, 212, 243
Glyceria ramigera, 155, 232
Glycine soja, 309
Gossypium arboreum, 154
— *herbaceum*, 203, 204
— *hirsutum*, 204
— *neglectum*, 204
Gueriniella serratula, 295
Helianthus annuus, 301
Hibiscus cannabinus, 208
— *sabdariffa*, 211
Hordeum vulgare, 233
Hyphaene schatan, 155, 184
— *thebaica*, 155
Ilex aquifoleum, 280
— *maté paraguarensis*, 213
Indigofera linifolia, 211
Ipomoea orizabensis, 250
— *purga*, 230
Irvingia barteri, 281
— *gabonensis*, 281
— *malayana*, 280
— *oliveri*, 280
Jasminum grandiflorum, 317
— *odoratissimum*, 318
Jatropha curcus, 258
Juniperus chinensis, 248
— *communis*, 246
— *occidentalis*, 247
— *rigida*, 247
— *sabina*, 155, 246, 247
Lactusa virosa, 6
Langsdorffia hypogoea, 245
Larrea divaricata, 214
— *tridentata*, 152
Lathyrus maritimus, 152
Ligustrum vulgare, 252, 255
Linum usitatissimum, 201, 234, 301
Lolium perenne, 155, 233
Lygeum, spartium, 155
Mallotus philippinensis, 249
Marrubium vulgare, 215
Medemia nobilis, 184
Medicago sativa, 155, 217, 233, 236
Melia azadirachta, 322
Mertensia maritima, 152
Metroxylon sp., 156
Moquina hypolenca, 252, 263
Moringa aptera, 321
— *oleifera*, 321
— *pterygosperma*, 321
Morus rubra, 252
Musa acuminata, 242
— *corniculata*, 242
— *paradisaica*, 242
— *simiarum*, 242
— *textilis*, 154, 207, 242
— *zebrina*, 242
Muscari botryoides, 320
Myrica arguta, 277
— *californica*, 275, 276
— *carolinensis*, 275, 276
— *cerifera*, 270, 275, 276, 277
— *cordifolia*, 278
— *hartwegi*, 276
— *jalapensis*, 277
— *pensylvatica*, 270, 275
— *quercifolia*, 278
— *xalapensis*, 277
Myristica angolensis, 291, 292
— *bicuhyba*, 292
— *canarica*, 292
— *fragrans*, 291, 292
— *malabarica*, 292
— *ochocoa*, 291
— *otoba*, 291, 292
— *platyferma*, 291, 292
— *scyphocephalium*, 292
— *sebifera*, 291
— *surinamensis*, 291, 292
Myroxylon pereirae, 296
Nephelium lappaceum, 310
Nerium indicum, 264
— *odorum*, 264
— *oleander*, 264
Nipa fruticans, 156
Oryza sativa, 234, 237
Oxycoccus macrocarpus, 282
Palaquium gutta, 23
Palythoa mamilosa, 194b
Panicum miliaceum, 234
Papaver somniferum, 295
Parthenium argentatum, 269
Pavia rubra, 266
Pedilanthus aphyllus, 154, 185
— *pavonis*, 154, 184, 185, 191
Pelvetia wrightii, 344
Persia pubescens, 152
Philadelphus coronarius, 319
Phleum pratense, 19

Plants, *Continued*
Phoenix dactylifera, 156
Phragmites communis, 231, 358
Phytelephas macrocarpa, 156
Picea abba, 259
— *canadensis*, 259
— *excelsa*, 155, 246, 266
Pinus caribaea, 247
— *ponderosa*, 247, 252
— *strobus*, 247
— *sylvestris*, 155, 246
— *thunbergi*, 247
Pirus malus, 288
Polianthes tuberosa, 320
Pongamia glabra, 322
Portulaca oleracea, 151
Primula farinosa, 152
Prunus armeniaca, 289
— *avium*, 289
— *domestica*, 289
— *mume*, 290
— *serotina*, 290
Pseudotsuga taxifolia, 252, 259
Pycnanthus kombo, 291
Pyrus communis, 289
Quercus crispula, 280
— *dumosa*, 200
— *suber*, 51, 255, 256
Raphia redunculata, 154, 156, 183
— *ruffia*, 183
— *vinefera taedigera*, 183
Rhododendron hymenanthes, 287
Rhus succedanea, 270
— *trichocarpa*, 270, 273
— *vernicifera*, 270
Robinia pseudoacacaia, 266
Rosa centifolia, 315
Rubus sp., 280
Sabal palmetto, 155
Saccharum officinarum, 155, 217, 218
Salix groenlandica, 152
— *purpurea*, 266
Salvia officinalis, 212
Sambuscus nigra, 255
Santalum album, 155, 245
Sapium sebiferum, 310, 311
Scheelea martiana, 178
Sarcocalla sp., 152
Sasa paniculata, 155, 242
Scheelea martiana,
Scirpus lacrustis, 233, 358
Secale cereale, 151, 234
Sempervivum acuminatum, 154
Serenoa repens, 175
Sesamum indicum, 309
Simmondsia californica, 48, 302
Soja hispida, 309
Sorbus aucuparia, 280
Sorghum halepense, 234
— *vulgare*, 155, 217
Spagnum sp., 358
Spartium junceum, 154, 210, 319
Spiraea ulmaria, 310
Stillingia discolor, 311, 312
— *sebifera*, 310, 311
Stipa tenacissima, 155, 217, 230
Syagrus coronata, 178
Syringia vulgaris, 319
Tabernaemontana sphaertcarpa, 268
— *utilis*, 78
Taraxacum officinale, 251, 267
— *vulgare*, 251
Taxus sp., 151
Terminalia catappa, 265
Thea japonica, 212
— *sasanqua*, 212
— *sinensis*, 212
Theobroma cacao, 155, 265
Thuja occidentalis, 155, 246, 247, 280
Tillandsia usneoides, 211
Toxicodendron succedaneum, 270, 273
— *trichocarpum*, 270
— *vernicifera*, 270, 273
— *vernicifluum*, 270
Tragopogon pratensis, 267
Trifoleum incarnatum, 206, 233, 319
— *repens*, 78
Triticum aestivum, 155
— *junceum*, 152
Tsuga mertensiana, 151
Tulipa sp., 151
Ulmus campestris, 266
Uva ursi, 214
Vaccinium macrocarpum, 270, 282, 287
— *oxycoccus*, 152
— *uliginosum*, 152
— *vitas-idaea*, 270
Viola odorata, 316
Vinca minor, 212
Virola bicuhyba, 291
— *guatemalensis*, 291

Plants, *Continued*
— *otoba*,
— *sebifera*, 291
— *surinamensis*, 291
— *venezuelensis*, 291
Viscum album, 279
Vitis labrusca, 290
Ximenia americana, 290
Zea indurata, 308
— *mays*, 233, 307
Plant waxes, ecology of, 151–152
formation of, 7–8, 152–153
Plastmalogen, 329
Plasters, 141, 815
Plastic objects, wax polishing, 754, 831
Plastic resins, use of wax with, 577
Plasticizer, wax as a, 451, 537
Plastics molding equipment, lubricant for, 547, 577, 578
Plastigels, 579
Playing card finishes, 780
"Pliofilm," 515, 638, 800, 803
"Pliolite Resin," 512–513
"Pliolite-Wax," 514–515
"Pliowax," 512–514, 732
Polenske number, 600
Polishes, automobile, 823–825
emulsion type, 720, 822–823
floor, 709–711
furniture, 825–827
leather goods, 747
liquid stove, 829
metal, 831
nonabrasive paste, 825
performance tests for, 724
resin-wax type of, 720–721
rubless floor, 721
silicone, 829, 830
water cream, 848
Polish industry, consumption of waxes in, 726
Polybutene, 504
Polybutene-polyethylene-wax blends, 508–509
Polybutene-wax mixtures, 504, 811
Polyesters, 67
Polyetholides (estolides), 62
Polyethanolamine stearate,
Polyethylene, 445–446, 803
manufacture of, 446
Polyethylene glycol esters, 489
— -polyisobutylene blends, 803
— polyol esters, 490
— resins, 445
— -wax concentrates, 516
— -wax mixtures, 506–508, 516–518, 802
Polyethylene waxes, 447–449
emulsifiable, 499
nonemulsifiable, 445, 448–449
physical properties of, 447
uses of, 172, 449, 690, 695, 785, 834, 864
Polyethylene wax-resin, definition of, 445
Polyhydric alcohol esters, 443, 464, 534–535, 680
Polyisobutylene-polyethylene plastic waxes, 509, 802–804
Polyisobutylene-resin-wax blends, 804
"Polymekon"-wax blends, 500–501
Polymethylene acid alcohols, 62–63
— hydrocarbons, 15
Polyol ether-esters, 449, 490
Polyoxyethylene fatty acid esters, 733
— sorbitol derivatives, 491, 670, 676, 685
Polypentaerythritol ester complex, 493
Polystyrene, 754
alkylated, 353, 518
Polystyrene-wax mixtures, 518
Polyvinyl resins, 452, 577
Ponderosa bark wax, 252–254
Portraits in wax, 773–774
Potdevin waxing machine, 793
Potting compounds, electrical, 429, 487, 694, 696
Pour point depressants for lube oils, 480, 645
Power and loss factors of waxes, 434, 890
Precision casting, wax in, 770–772
Preventing oxidation of wax melts, 439
Printing and labelled paper, 794
Printing inks, 833 *et seq.*
Prints, spray waxing of lithographed, 755, 780, 793
Propolis, 97, 100
Proporesins, 100
Propylene glycol palmitates, 535
— — stearates, 535
Protective cream, 676
Protective paper packaging, 781
"Protowax," 676, 819

Proto- and pyroparaffins, 355
Prune skin wax, 289
Prunus waxes, 289
Pseudosterols
  agnosterol, 27, 135, 137
  alpha-sitosterol, 30
  androsterol, 251
  ariseasterol, 28
  cafestol, 312, 313
  dihydrolanosterol, 136
  homoandrosterol, 251
  homotaraxasterol, 251
  isocholesterol, 136, 139
  kahweol, 312, 313
  lanosterol, 27, 135, 136, 137
  oleasterol, 265
  taraxastol (taraxasterol), 29, 251
Pyrobitumens, 342
Pyrolysis of waxes, 89
Pyropissite, 346
Pyrotechnics, 707–708

Quaternary ammonium salts, 524

Radio condensers, wax for, 695
Raffia wax, 183
Raffinates, wax bearing, 378 *et seq.*
Rambutan seed wax, 310
Raspberry oil, wax from, 280
Ration boxes, waxing, *see* Field ration packages
Rayon, wax finishing, 855
Razor-strop dressing, 747
Reeds, wax of, 231
Refractive index, determination of, 615
  of beeswax, 82
  of carnauba wax, 164
  of hydrocarbons, 12
  of monoethanoid acids, 44
  of refined paraffines, 410
  of various waxes, 883
Regenerated cellulose, *see* Cellophane
Reichert-Meissl number, 198, 583, 600
Replacement waxes, 172, 177, 522
Resenes, 70, 71
Resin (resinolic) acids, 70, 117, 207
Resinols (resin alcohols), 70, 117
Resino-tannols, 70, 100
Resins, acid values of natural, 71
  commercial, 511, 530, 804
  computation of amount of, 71
  melting points of natural, 71
  natural, 70, 199
  terpene, 801–802
Resin-wax coating compositions, 796, 801
Resin-wax mixtures, 511
Retamo wax, 196
"Rezo Wax," 494, 495, 713, 719
Rhimba tree, wax of, 216
Ribbon inks, 813
Ricebran wax, 237 *et seq.*, 847
Rice wax, hydrogenated, 241
"Rilan Wax," 526
Rimu wood, wax of, 200
Rod wax, 388, 390
Root fats, 249
Roots, waxes in, 250
Rose wax, *see* Flower waxes
Rosin, 71, 789, *see also* Colophony
  hydrogenated, 71, 802
  oil pitches, 647, 649
Rubber adhesives, 637, 639, 642
Rubber articles, use of paraffine in, 749
Rubber crepe, use of wax with, 750
Rubber flooring composition, 750
Rubber gaskets, 751
Rubber goods, finishes for, 544
  mold release agents for, 749
Rubber hydrochloride, 638
Rubber latex, use of wax in, 752
Rubber molded goods, use of stearine in, 731
Rubber softeners, 749
Rubber sunproofing, 751, 752
Rubber-wax blends, coatings of, 792, 795
Rubber, sponge, 753
  synthetic, 751
Rubless polishes, 721
Russian white oil, 420
Rust inhibiting wax emulsions, 544
Rust preventatives, 642, 643, *see also* Anti-rust composition
Rye grass, wax of, 233

Saddle soap, 746
Safety explosives, 705
Safflower, wax of, 300
Salves, 819
Sandal leaves, wax of, 245
Sandsedge, wax of, 233
"Santowaxes," 493
Sapogenic waxes, 298, 299, 736

Saponification equivalent, 586
Saponification number, definition of, 584
Saponification number, determination of, 584–586
Saponification number by Hezel method, 190, 360, 585–586, 894
Sapropelites, 344, 346
Saran, 729, 800, 803
Sausage, wax coating for, 733
Saw palmetto wax, 175
Saxon-Thüringien paraffins, 372–373
Scale insect waxes, 104 *et seq.*
Scale wax emulsions, 528, 543–544
Scale wax oils, 400–401
Scale waxes, 397–398
Scottish shale oil, paraffine from, 373–374
Scrub oak leaves, wax of, 200
Sealing strength measurements, 783
Sealing tapes, 840 *et seq.*
Sealing wax, 840 *et seq.*
  electrical, 487, 692, 696–697
"Sealz Waxes," 515, 845
Seaweed wax, 343
Sedges, waxes from, 217, 232–233
"Seekay Waxes," 452, 457
Selective solvent dewaxing process, 421–423
Selective solvents, 391, 422, 423
Self-seal wax paper, 782
Senna, wax of wild, 212
Serviceberries, wax of, 280
Sesame seed oil wax, 309
Setting points, det'n of, 602 *et seq.*
"Seycowax," 527
Shale-oil wax distillate, waxes from, 372 *et seq.*
Shampoo, liquid, 547, 684–685
Sharples centrifuge, 418, 419
Shaving cream, brushless, 685
Shaving soaps and powders, 686
Shellac wax, 109 *et seq.*
  uses of, 527, 695, 696, 748, 851
Shell powder, 705
Shipways, wax for, 438, 759–760
Shoe creams, *see* Shoe polish pastes
Shoe dressings, 747
Shoe polish pastes, 846 *et seq.*
Shoe stiffner, 748
Shoe stitching wax, 747
Shoe wax stains, 747
Shoemaker's sewing wax, 747
Shoemaker's thread wax, 747
Shore durometer hardness, 611
Shot shell tubes, paper, 706
Show-card transparencies, 642
Shrinkage of waxes, 411, 613, 615
Shuffleboard wax lubricant, 759
Silica, colloidal, in floor waxes, 710
Silicone oils, 519, 829
Silicone polishes, *see* Polishes, silicone
Silicone-wax compositions, 518–519
Silicon wax, 489
Silos, wax-stone, 862
Silver polish, 831
Sisal-hemp wax, 208–210, 847
Ski wax, 757 *et seq.*
Slack wax, 394, 395, 398, 526
  sweating of, 395
"S-Polymer," 509
Slip resistance determination of, 724
Slip varnish, 857
Slitter and rewinder, paper, 794
Slop oil, 380, 394, 399, 421, 425
Slop wax, 388, 393
Slushing oils, 577, 643
Smokeless powder, wax in, 705
Snow brush wax, 198, 199
Soap, shaving, *see* Shaving soap
  superfatting, with lanolin, 129
  wax in, 149, 274, 526, 686
Soap from synthetic acids, 555
Soda straws, 438
Softening point, determination of, 605 *et seq.*
Solar extraction process, 78–79
Solidification point, det'n. of, 607–608
Solidified alcohol, 663
Solubility tests on waxes, 83, 623–624
Solvent-aides, 385
Solvent binding power of waxes, 713
Solvent dewaxing plants, 381
Solvent retention by waxes, 714 *et seq.*
Solvent uptake by waxes, 712
Solvents, flash and fire points of, 827
  naphtha, type of, 828
Sorbitan esters, 491, 669, 735
  — monostearate (Span) 491, 735; *see also* "Spans"
Sorghum grain wax, 234
Sound records, use of wax in, 438, 852–854
Soybean wax, 309

"Spans," 491, 540, 677, 735
Spanish moss, wax of, 211
Specific gravity, determination of, 610–611
Specific inductive capacity, *see* Dielectric constants
Specific rotation, determination of, 625–626
Spermaceti, 146 *et seq.*
  uses of, 144, 668, 671, 679, 746, 752, 863
Spermaceti candles, 654
Spermaceti cerate, 144
"Spermafols," 474
Sperm oil (sperm-head oil), 146 *et seq.*
  hydrogenated, 148, 755
  sulfurized, 756
  uses of, 149, 533, 755
Sponge rubber, use of wax in, 753
Sponges, components of, 27, 28, 46
Squalene, 16, 241, 324
Squeeze mold casting, 776
Stearamide, 482, 660, 855
  derivatives of, 484 *et seq.*
Stearanilide, 444, 486
Stearic acid, commercial, 556 *et seq.*
  consumption of, 561
  uses of, 561–562, 657, 658, 671, 751, 752, 864, *see also* Acid, stearic
Stearin, 70, 556, *see also* Triglycerides
Stearin pitch, 130
Stearine, 556, *see also* Stearic acid, commercial
Stearolactone, 61, 659
Stearone, 444, 476, 478–479, 494, 643, 660, 713
Stearyl alcohol, commercial, 547, 667, 686
  phosphated, 548
  uses of, 668, 681, 687, 688, 807, *see also* Alcohol, stearyl
Stearyl hydroxystearate, 568
  myristate, 68
  octadecanoate (Stearyl) stearate, 68, 494
  palmitate, 68
Steatinums, 816
Stencil films, heat resisting, 812
Stereoisomerism of acids, 48
Sterol ring structure, 29
Sterols, 26 *et seq.*
  analysis of, 28, 596 *et seq.*
  animal, 28
  chemical structure of, 29
  dihydro, 26, 27, 28
  esters of, 28, 235, 308
  individual
    agnosterol, *see* Pseudosterols
    bombicesterol, 121
    brassicasterol, 228
    carbisterol, 27
    cholesterol, 27, 29
      determination of, 598
      occurrence of, 121, 137, 143, 147, 150
      properties of, 27, 28, 672
      uses of, 668, 672, 674
    clionasterol, 28, 30
    coffeasterol, 312, 313
    coprosterol, 150
    dihydrocholesterol, 27, 28
      — sitosterol, 26, 27, 241, 308
      — stigmasterol, 27, 28, 30
    ergosterol, 26, 29, 137, 323
    fucosterol, 26, 343
    Hess' phytosterol, 254
    homolestranol, 29, 265
    nimbosterol, 322
    oleastranol, 29, 265
    ostreasterol, 28
    paracholesterol, 28
    pelvesterol, 344
    sitosterol, 26, 27, 30, 228, 241, 265, 266, 268
    spongasterol, 27
    stigmasterol, 27, 28, 30, 228, 241, 265, 309, 313, 598
    undesterol, 216
    zymosterol, 26
  method of determination of, 596 *et seq.*
  occurrence of, in cane wax, 228
  qualitative check tests for, 598
  role of, in lipid waxes, 26
Stick-lac, 104, 113
Stick lubricants, 643, 753, 757
Sticky flypaper, 640
Sticky wax, 778
Stillingia tallow, 312
Stingless bee wax, 101
Stitching machine wax, 749
Stove polish, 829
Straw wax, 234
Strontium stearate, 572, 577
Stuffing grease for leather, 744

Succulent plants, waxes of, 154
"Stroba Wax," 494
Suberin, 255
Sugarcane oil, 220, 225
Sugarcane wax, 217 *et seq.*
  properties of, 227
  uses of, 229–230, 665, 667, 814, 847
Suint, 122
Sun-checking of rubber, 751
Sunflower seed wax, 301
Sun-preventive (sun-screening) creams, 103, 141, 674, 677
Sunproofing agents for rubber, 751, 752
"Superla Wax," 428, 700
Suppositories, 141, 548, 564, 819
Surakhansk cerasin, 355
Surface-active agents, 295, 524, 539–541
Sweater house, 395, 399
Sweating of wax distillate, 399
Sweat wax, 395, 397
Sweeping compounds, wax in, 757
"Syncera Wax," 751
Synthetic emulsifiable waxes, 443
Synthetic fatty acids, 553–555, 566–567, 568
Synthetic paraffin wax, 444, 463
Synthetic wax alcohols, 474, 544 *et seq.*
Synthetic wax esters, 461, 462, 463 *et seq.*, 481, 494, 547
Synthetic waxes, 443 *et seq.*

Tablet polishing, 821
Tailor's dummies, 753
Tallow dips, 652, 653
Tank-bottom wax, petroleum, 426
Tanks, wax coating concrete, 861
Tank-car handling of wax, 417
Tape, adhesive waxes, 637, 640
Tapers, wax, 352, 654, 655
Taraxasterol, *see* Pseudosterols, individual
Taut-pressed oil, 148
Tavern candles, 662
Tea wax, 212
"Teflon," insulation,
Telephone switchboard wire insulation, 697
Telemerization, 495
Temperature conversion tables, 894
Tensile strength, determination of, 616
  effect of addition of oil on, 409
Tent cloth, fireproofing, 856
  waxing, 397, 856
Termiteproofing, 796
"Tervan Waxes," 510, 804
Textile industry, use of wax in, 854 *et seq.*
"Textile proofers," 398
Textile softeners, 527, 538, 854, 855
Thermometers, etching of, 104
"Thermold," 754
Thermoplastic wax material, 512, 772
Thompson copy-prints of printings, 769
Thread, waxing of, 397, 398, 846
Tin-plate fabrication, 474
Tissue creams, 673
T.N.T. explosive, 704, 705
Tobacco, waxing of, 856
Transfer inks, 838
Tree-bands for insect control, 844
Tree wax emulsion, 844
Tree waxes, 844
Triethanolamine (T.E.), 738, 756, 823, 824, 855, 865
Triethanolamine stearate (T.E.S.), 531, 823, 824
Triglycerides, 67, 69, 70
  melting points of simple, 69
  molecular weights of, 70
  role of mixed, 67
  saponification numbers of, 70
  x-ray spacings of, 69
Trigona (Trigonen) wax, 88, 101
Trihydroxystearin, 70
Trilaurin, 69, 281, 294
Trimethylene glycol esters, 535
Trimyristin, 69, 281, 294
Tripalmitin, 69, 95, 153, 536, 663
Tristearin, 536
Triterpene alcohols, 136, 598
Trolleys, waxing of, 756
Tubercle bacillus waxes, 306, 324 *et seq.*
Tuberculoprotein wax, 328
Turpentine absorption by waxes, 712 *et seq.*, 847
Turtle oil cream, 674
Tusaud wax works, 2
"Tweens," 491, 540, 677
Twitchell process, 549
Typewriter ribbons, 439, 813
Typographic inks, wax in, 834 *et seq.*

Ubbelohde melting point, 604
Ucuhuba wax (fat), 291–293
Umbelliferone, 299, 300
Unguents, 172
Unit cell crystal structure, 13, 36–38, 53
Unsaponifiable matter, det'n of, 589–590
Unsaturated hydrocarbons, 16 *et seq.*
Unsaturated fatty acids, 44 *et seq.*
Uricury wax, *see* Ouricury wax
Ursolene, 283, 284, 285, 286
Ursolic acid, *see* Acid, ursolic
Urson, 279
Utah ozocerite wax, 353–354
"Utahwax," 347, 348, 353, 713, 746, 814
Urva ursi wax, 214

"Vaccinol," 288
Vacuum distilled waxes, 498
Vacuum still process, 379
"Vanidiset Resin," 649
Vanishing cream, 671
Varnishes, use of wax in, 857, 858
"Vaseline," 349, 418–419, 819
Vegetables, waxing of, 737 *et seq.*, 741–742
Vegetable tallows, 11
Vigil lights, 658
Vinyl-copolymer resins, 451, 796, 801
Violets, wax of, *see* Flower waxes
Violin strings, waxing, 752
Viscosities of waxes, table of, 871–874
Viscosity, absolute, 618
  determination of, 617–618
  kinematic, 618
"Vistanex," 505, 506, 509, 641, 802, 803, 804
Vitamins, 28, 590, 674
Volume contraction of waxes on cooling. 411
Votive lights, 658

Wall paper, wet waxing, 794
Water number, 687
Waterproofing
  bags, 397
  building material, 531, 861
  canvas, 398, 856
  cartons, 800
  cloth, 352, 855, 856
  coal pellets, 864
  krafts, 397, 398
  leather, 578
  masonry, 578
  paper and paperboard, 527, 779
  paper stock, 526, 532, 578
  powder bags,
  rope, 578
  shells, ordnance, 103
Waterproof label varnish, 858
Wax, derivation of the term, 1, 2
Wax acid bottles, 439
" adhesives, 637 *et seq.*
" -and-rubber compositions, 515
" -spray emulsions, 741
" bottle seals, 843
" coating machine, Greer's, 727
" colorings for fruit, 742
" components, formation of plant, 7 *et seq.*
" consumption in the United States, 3
" distillates, petroleum, 379 *et seq.*
" emulsions, *see* Emulsions
" esters, 63
" figures, 352, 439
" finishes
  for fabrics, 543, 544, 855
  for leather, 747, 748
  for metal and hardware, 544
  for rubber goods, 544, 751
" flaking machine, 472
" floor powder, 719
" flowers, 775
" formation in plants, 2
" gels, 715
" inhibitors to coarse crystals, 351
" laminants, 352, 438, 781
" leaf casting, 776
" lining cans, 651
" lubricating, stick-type, 755
" matches, 766
" matrix in printing, 769
" nonslip, 801
" oils, 400
" phenol depressants, 647
" portraits, 773
" printing, 774
" -resin emulsions, 520
" -resin mixtures, 511
" -rubber coatings, 515, 641
" -rubber mixtures, 515
" sculpture, 2
" sealing ability measurements, 783
" -set links, 838

Wax, *Continued*
" -soluble colors, 660, *see also* Dyes for waxes
" storage, 790
" tailings, 378
" telomers, 495
" -works exhibition, 2
Waxed glassines, *see* Glassines, waxed
"Waxed in," oil wells, 391
Waxes, animal, *see* Animal waxes
blended, 499
chemical components of natural, 2-3
classification of plant, 154
compounding of,
conifer, 246
earth, 342, 346
etholide, 53, 246
floral, *see Floral* waxes
fossil, 342, 343
from flowers, 313
from fruit hairs, 249
from fruits and berries, 269
from grasses and sedges, 217
from latex trees, 267
from leaves, 243, *see also* Palm tree waxes
from microörganisms, 323
imitation ceresin, *see* Imitation ceresin wax
insect, *see* Insect waxes
microscopy of, 407
natural, 76
preventing oxidation of melted, 439
synthetic, 443
Waxing
baking utensils, 732
berry hallocks, 743
enamelled ware, 726
fruits, 736
linoleum, 492
lithographic prints, 793
machine, 782, 793
match splints, 761, 763
methods, "dry" and "wet," 792
motor parts, *see* Motor parts, waxing
paper containers, 779, 781, 786, 787, 788, 798, 799, 800
paper and paperboard, 779, 780-790, 791-794
ration boxes, 800
thread, *see* Thread, waxing of
tobacco, 856
vegetables, 737-741
wrapping films, 794-796, 802-804
yarn, 439
Wax sticks, 755
Wax-stone silos, 862
Waxy acids, commercial, 548 *et seq.*
Waxy alcohols, commercial, 544 *et seq.*
Waxy ketones, commercial, 475 *et seq.*
Wet waxing, 780, 792, 793-794
Whale oils, ordinary, 180
Wheat blade, wax of, 234
White mineral oil, 420, 671, 674
White oleyl alcohol, 680
White petrolatum, 674, 687
White pine chermes, wax of, 247
White shoe cleaning paste, 849
White spruce wax, 259
White wax, 669, 818, *see also* Beeswax, white
Wild senna, wax of, 212
Window envelopes, 802
Wind torches, 662
Wire drawings, 574, 577
Wood impregnants, 453, 761
Wood stain, 172
Wool fat, *see* Woolwax
Wool fat olein, 129
Wool fat stearine, 129
Wool grease, 121, 837
Wool-grease soap, 129
Woolwax, 121, 122 *et seq.*
uses of, 527, 642, 643, 753, 835, 844, *see also* Lanolin, anhydrous
Woolwax alcohols, 140
Wrappers, for cakes, 785, 786, 790
for chewing gum, 785, 792
for fish, 733, 792
for fruit, 792
for milled soaps, 786
for potato chips, 792
for powdered milk, 785
Wrapping material, moistureproof, 796
WVP values of packaging materials, 804
WVTR values of various materials, 785